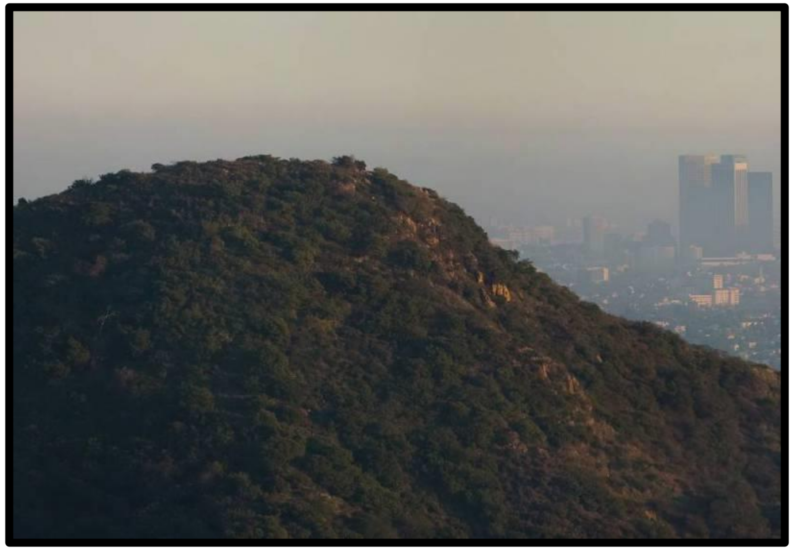
Chemical Product Emissions Emerging as Important Urban Source of Volatile Organic Compounds



Brian C. McDonald

CIRES

University of Colorado Boulder

NOAA

California Air Resources Board (April 19, 2019)

Acknowledgements

CIRES

University of Colorado Boulder

NOAA

Matt Coggon, Carsten Warneke, Jessica Gilman, Jeff Peischl, Ken Aikin, Justin DuRant, Joost de Gouw, Stuart McKeen, Tom Ryerson, Michael Trainer, Patrick Veres, Abigail Koss, Bin Yuan, Francois Bernard, Abigail Koss

Environment and Climate Change Canada

Alexander Vlashenko, Shao-Meng Li

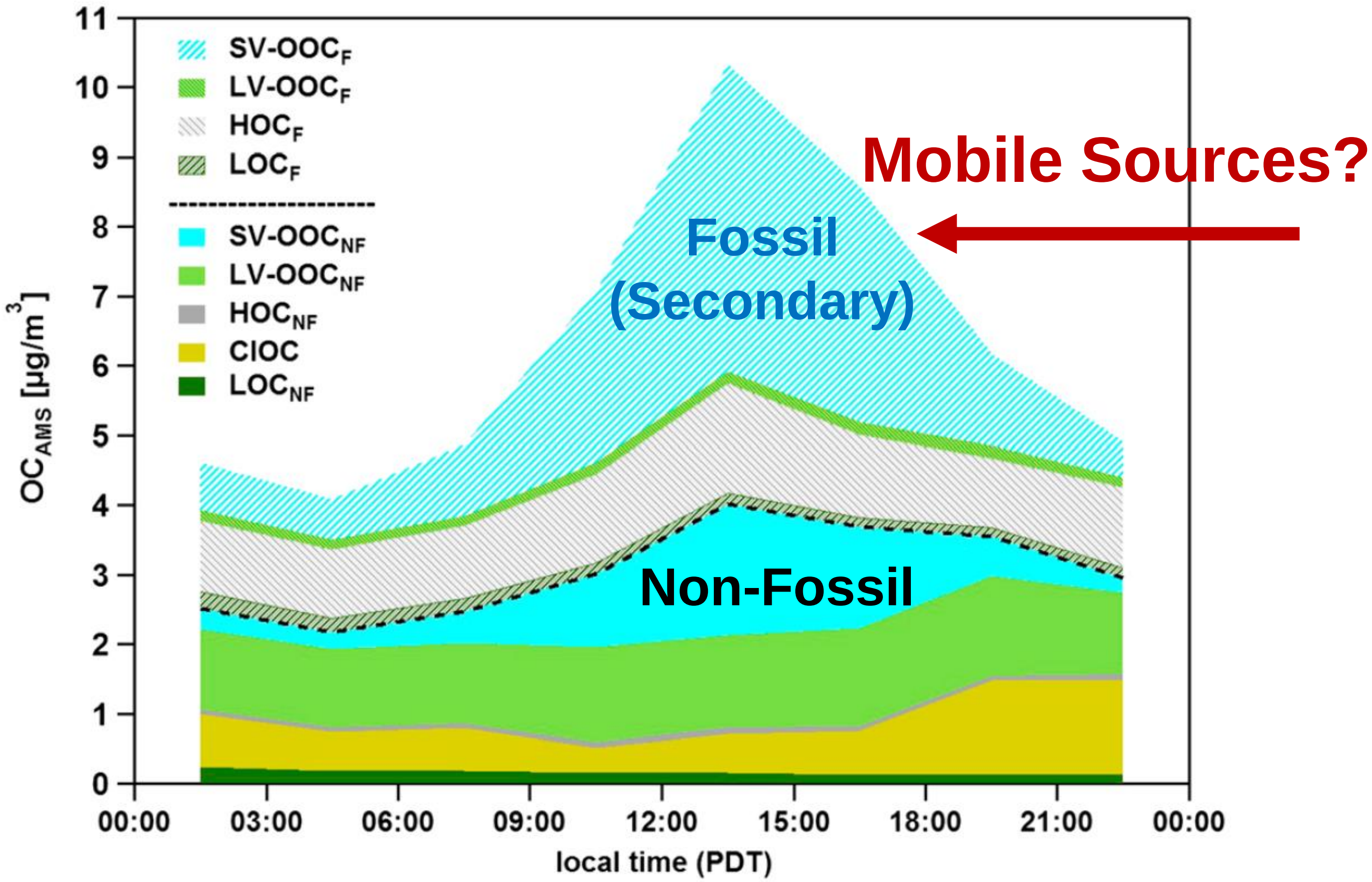
The City University of New York

Fred Moshary, Mark Arend

Funded by a CIRES Innovative Research Proposal and the NOAA Cooperative Institute Agreement.

Which Source Dominates Fossil SOA Formation?

Los Angeles 2010 (Pasadena)



^{14}C analysis of carbonaceous aerosol from Zotter et al. (*J. Geophys. Res.* 2014)

Bahreini et al. (*GRL* 2012)

- **Gasoline** emissions dominate in LA

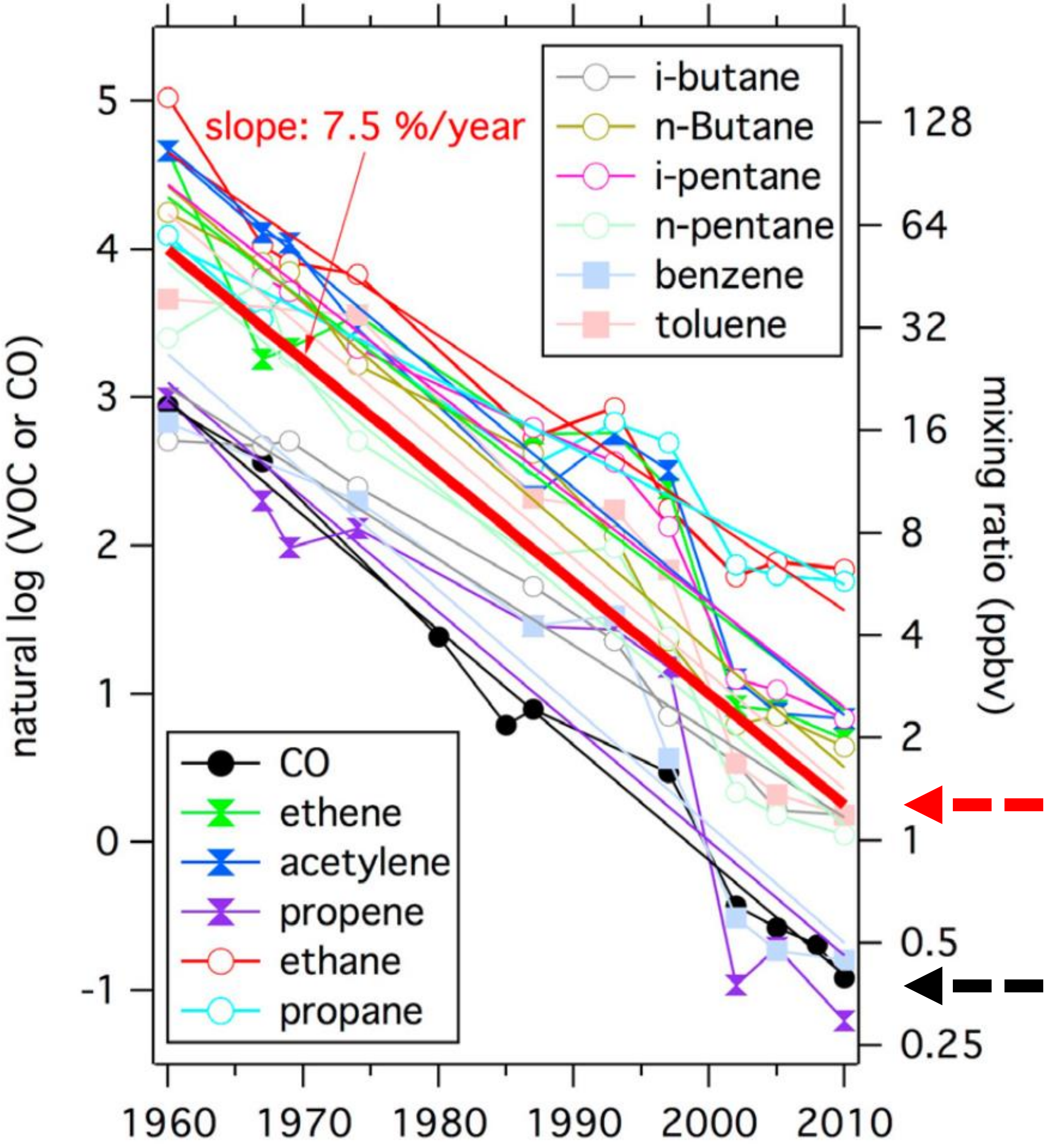
Gentner et al. (*PNAS* 2012)

- **Diesel** emissions dominate in LA

Ensberg et al. (*ACP* 2014)

- **Other sources** dominate, or
- **SOA yields** of vehicle emissions substantially underestimated

Long-Term Trend in Ambient VOCs (Los Angeles)



Gasoline VOCs Decreasing Rapidly

CO Decreasing Rapidly

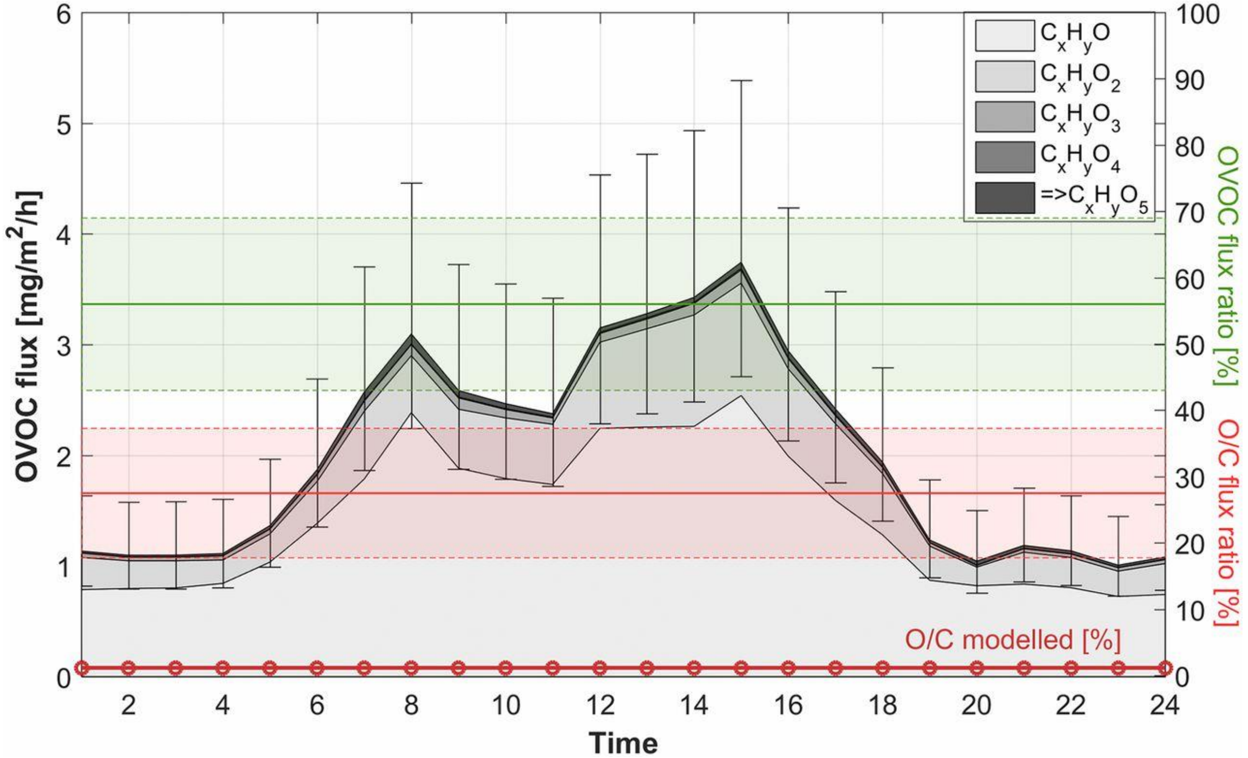
Warneke et al. (*J. Geophys. Res.* 2012)

Two Recent U.S. and European Studies on "Other" Sources

PNAS

Urban flux measurements reveal a large pool of oxygenated volatile organic compound emissions

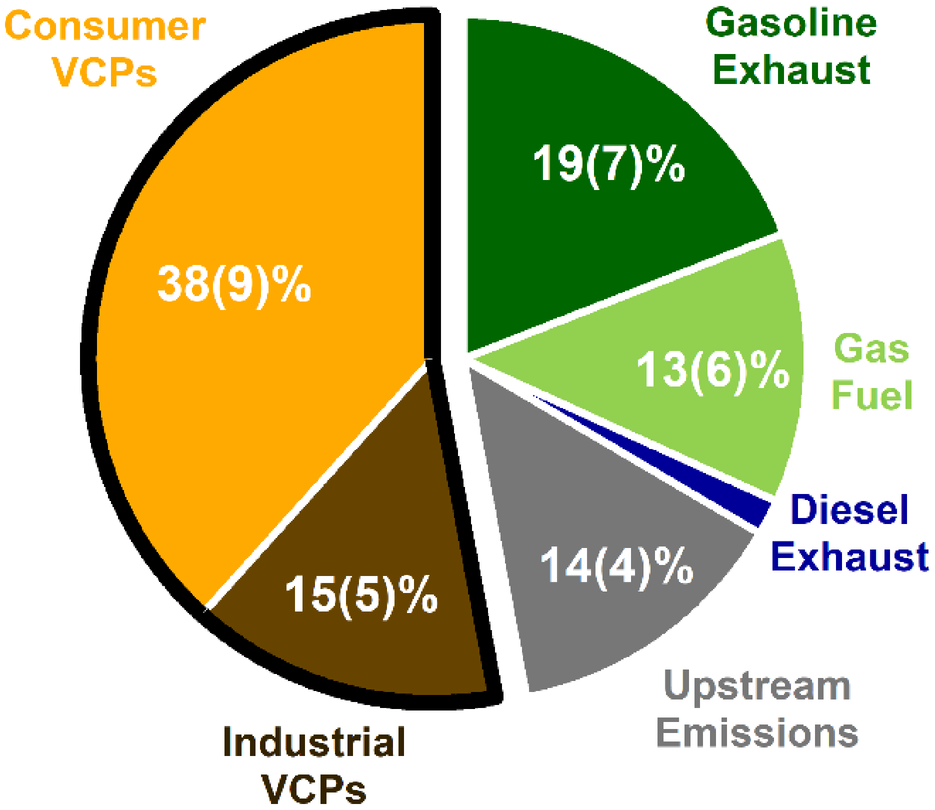
T. Karl[a,1], M. Striednig[a], M. Graus[a], A. Hammerle[b], and G. Wohlfahrt[b]



~50% of VOC emissions in Innsbruck, Austria emitted as oxygenated compounds, including emissions from solvents

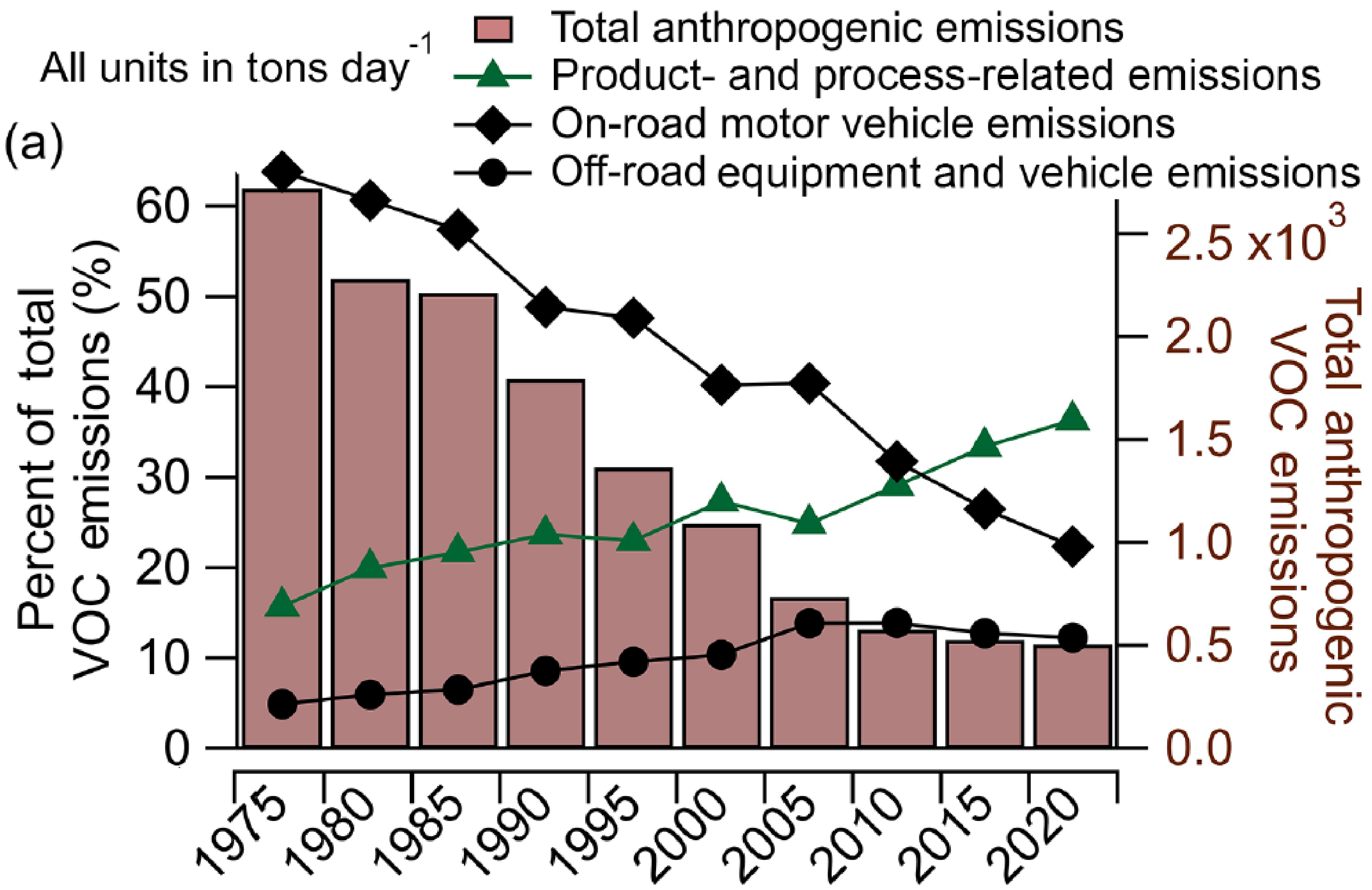
Science

Volatile chemical products emerging as largest petrochemical source of urban organic emissions



VOC Emissions = 350 ± 50 Gg

VOCs also Transitioning in CARB Inventories (Mobile Sources → VCPs)

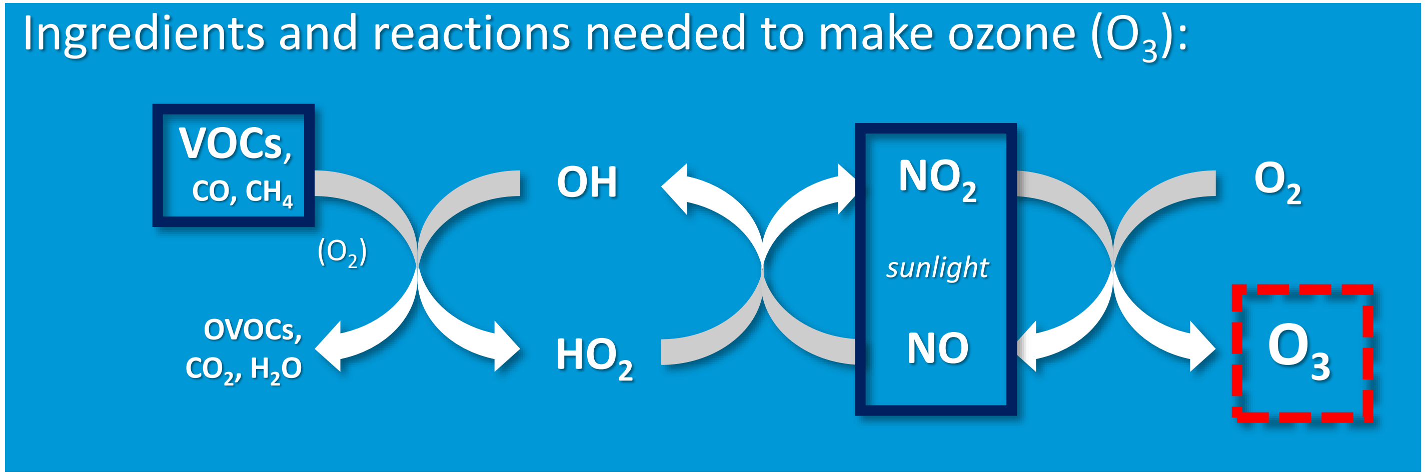


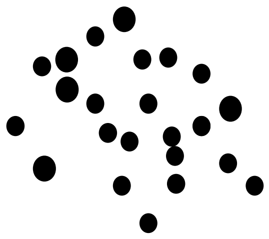
Similar trends for **SOA** and **Ozone** formation potential

Khare et al., "Considering the future of anthropogenic gas-phase organic compound emissions and the increasing influence of non-combustion sources of urban air quality", *Atmos. Chem. Phys.* 2018.

Natural and Human Emissions Impact Atmospheric Chemistry

Atmospheric chemistry





Secondary Organic Aerosol

Natural processes **Human activities**

Primary emission sources

Figure provided by Jessica Gilman (NOAA).

Research Objectives

(1) Identify chemical tracers for detecting VCP emissions in ambient air

- Establishing D5-siloxane as a tracer of personal care product emissions

(2) Quantify VCP emissions in another US megacity: New York City

- Field measurements of VOCs made in winter/summer of 2018
- Are VCPs a larger fraction of anthropogenic VOCs in denser cities?

D5-Siloxane an Atmospheric Tracer for Personal Care Products

Example antiperspirant/deodorant

ACTIVE INGREDIENTS

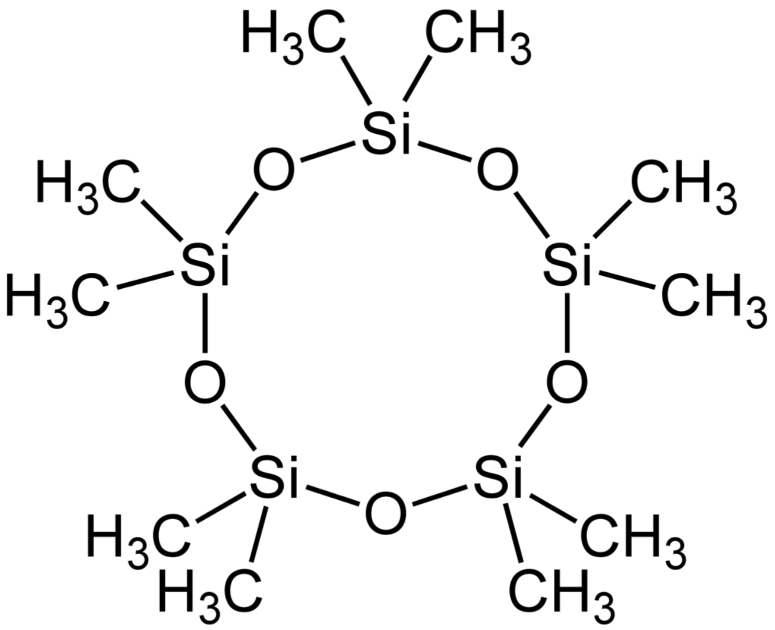
Aluminum zirconium octachlorohydrex Gly 16% (anhydrous)

INACTIVE INGREDIENTS

Water, alcohol denat., cyclopentasiloxane, propylene glycol, dimethicone, calcium chloride, PEG/PPG-18/18 dimethicone, fragrance

Antiperspirants ~70%

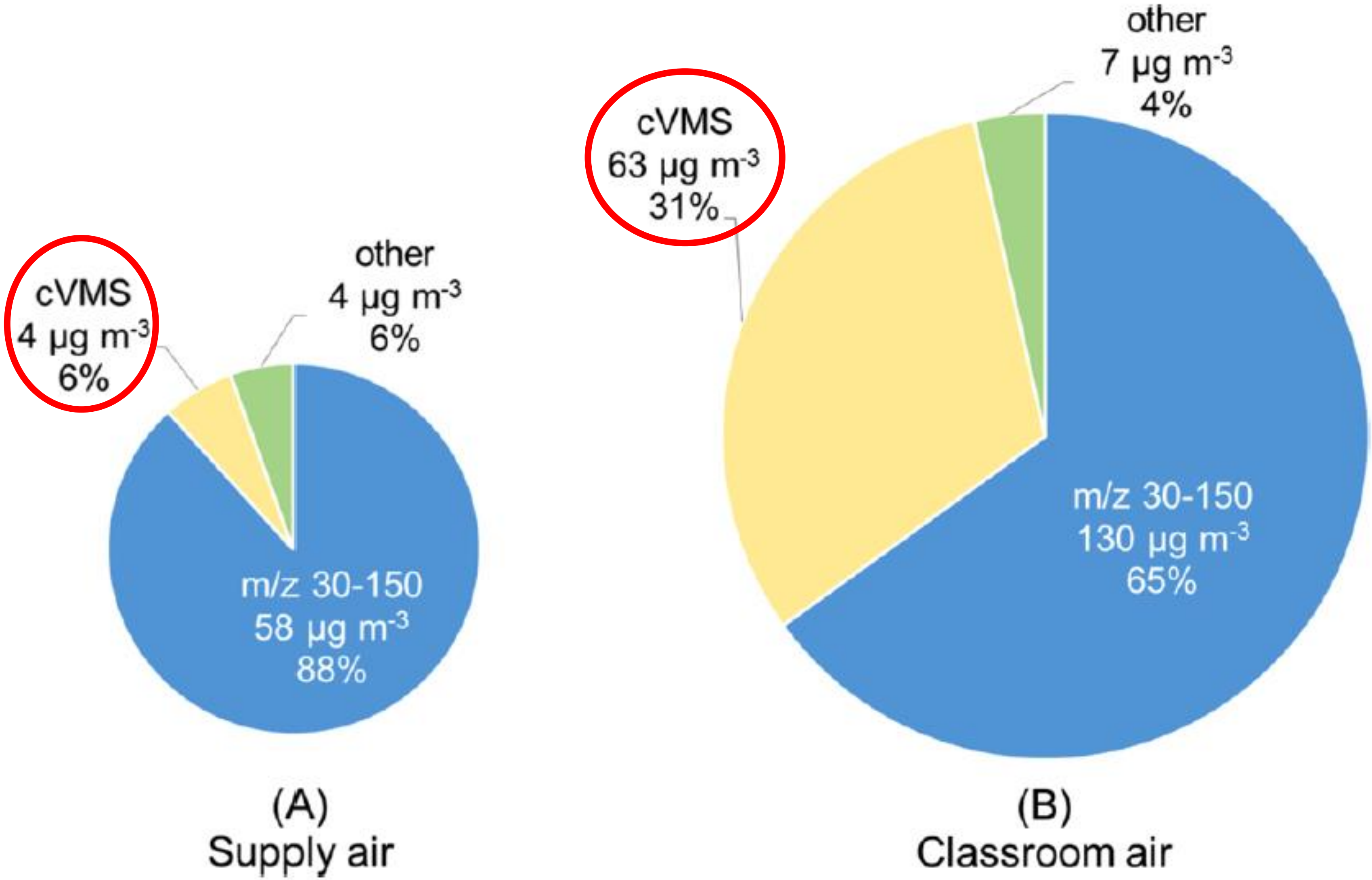
Hair care ~20%



Cyclopentasiloxane (D5-siloxane)

MacKay et al. (*Env. Tox. & Chem.* 2015)

Siloxane Concentrations Enhanced in Indoor Air (mostly D5)



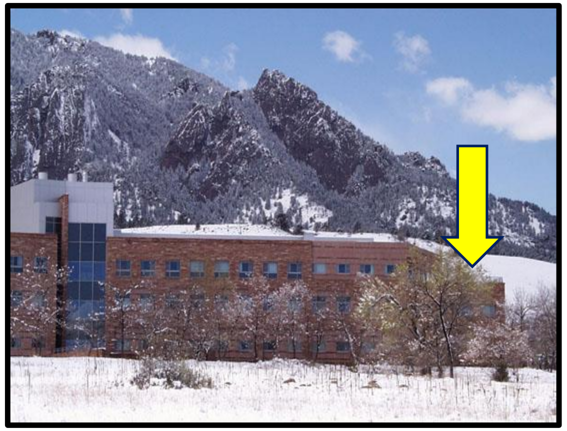
Siloxanes were most abundant VOC found in engineering classroom

100 – 700 mg/person/d

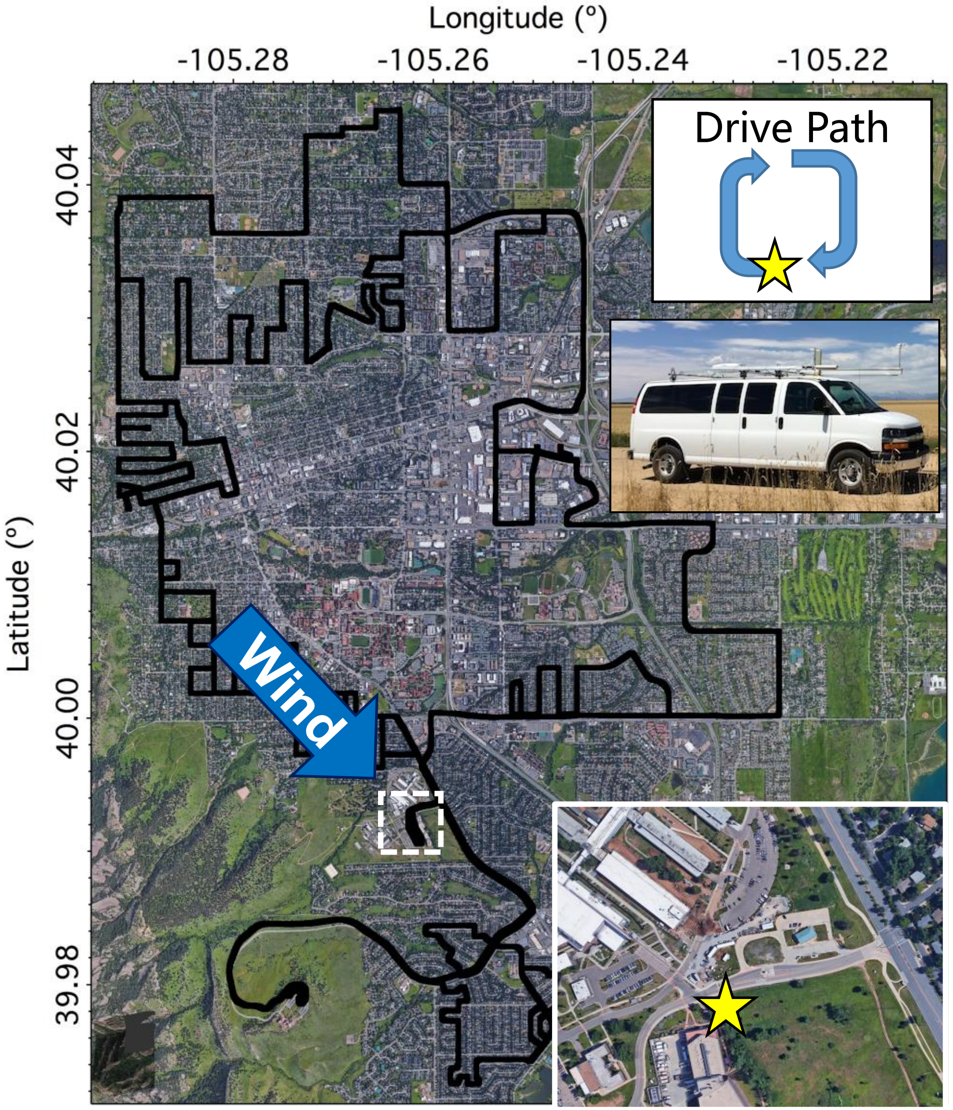
Tang et al. (*Environ. Sci. & Technol. 2015*)

Investigating D5-Siloxane in Boulder, CO

Ambient Sampling



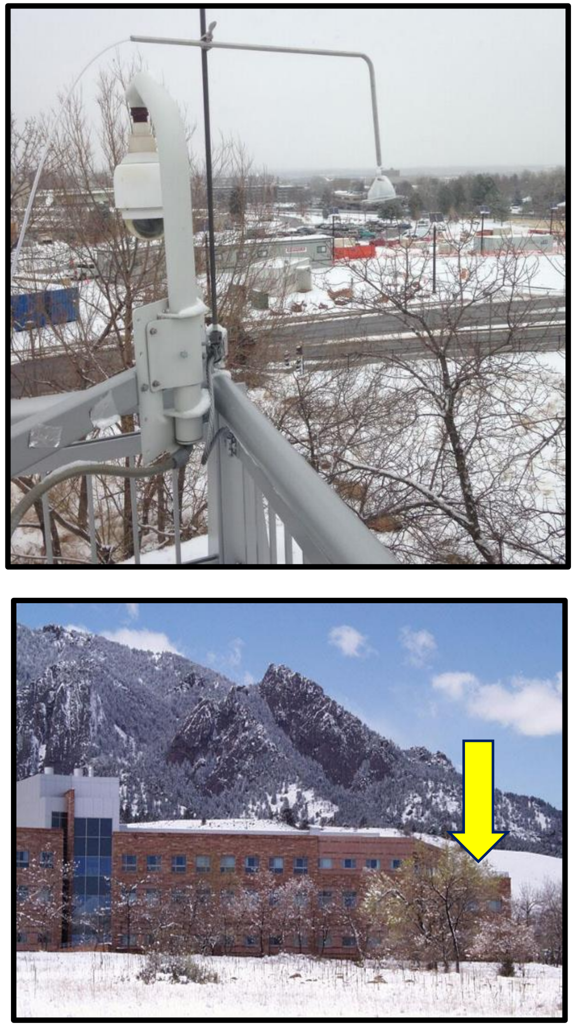
Mobile Sampling



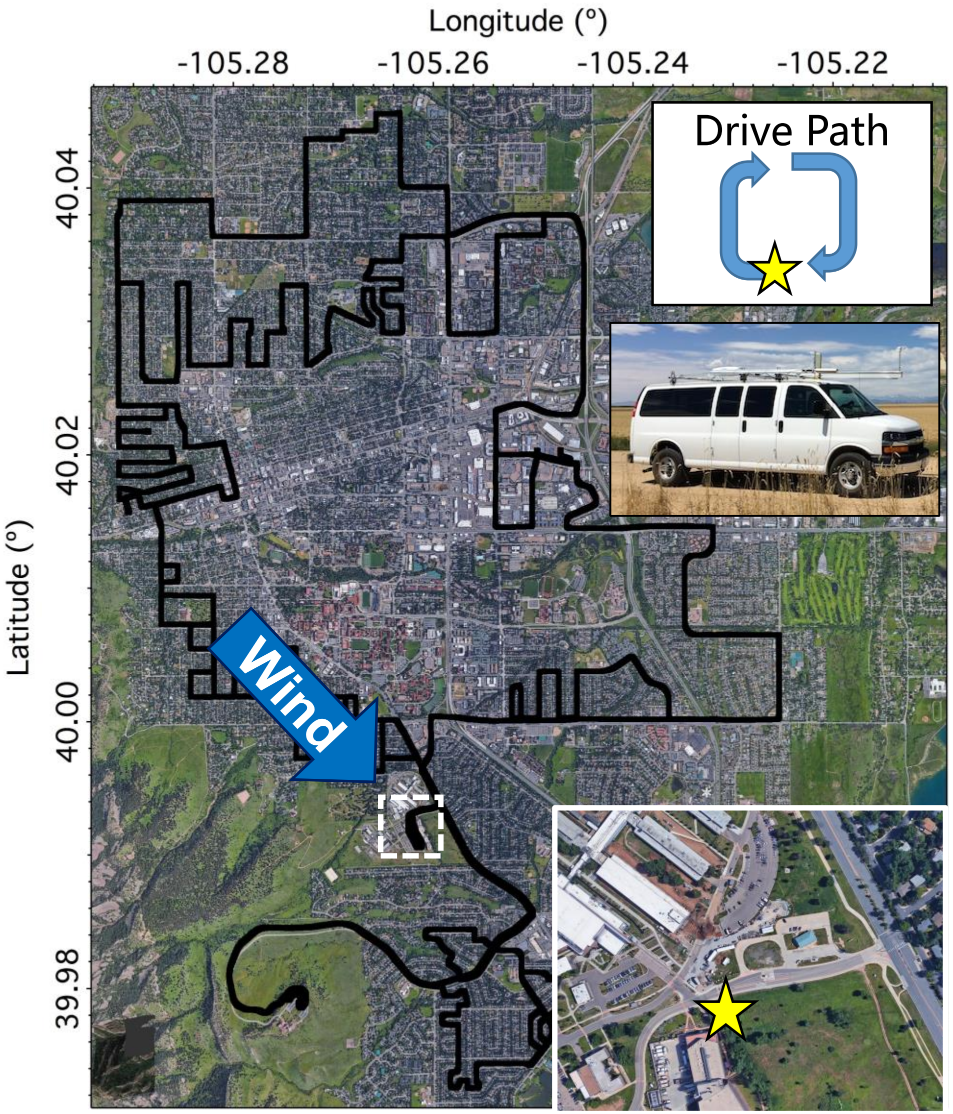
Matthew Coggon
(NOAA)

Investigating D5-Siloxane in Boulder, CO

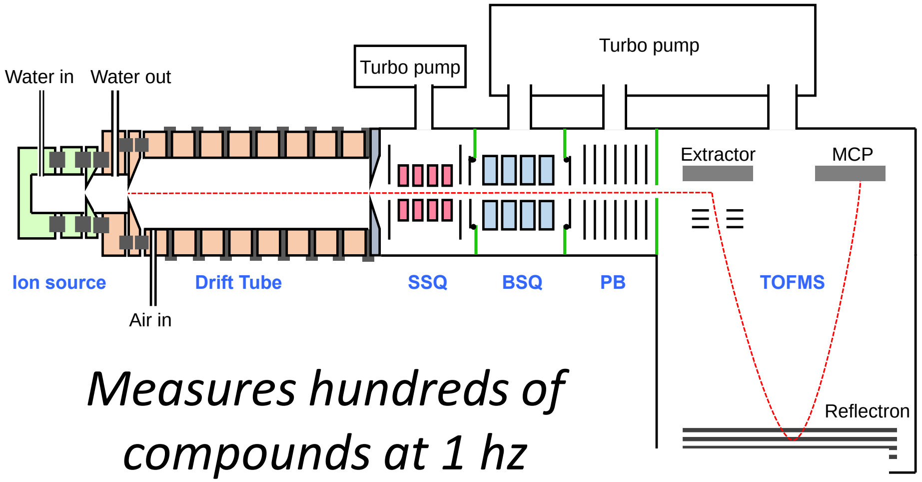
Ambient Sampling



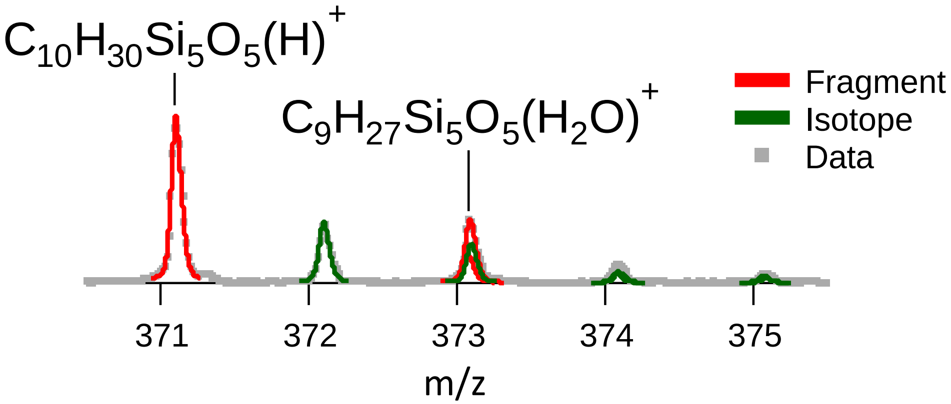
Mobile Sampling



PTR-ToF-MS

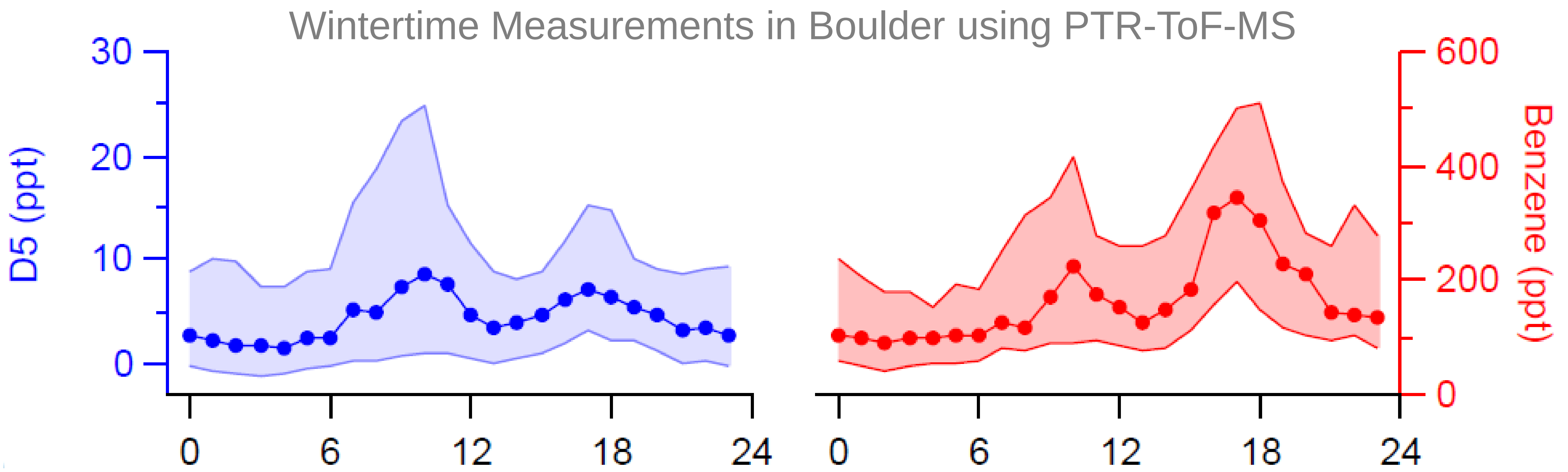


Measures hundreds of compounds at 1 hz



High sensitivity to D5 siloxane

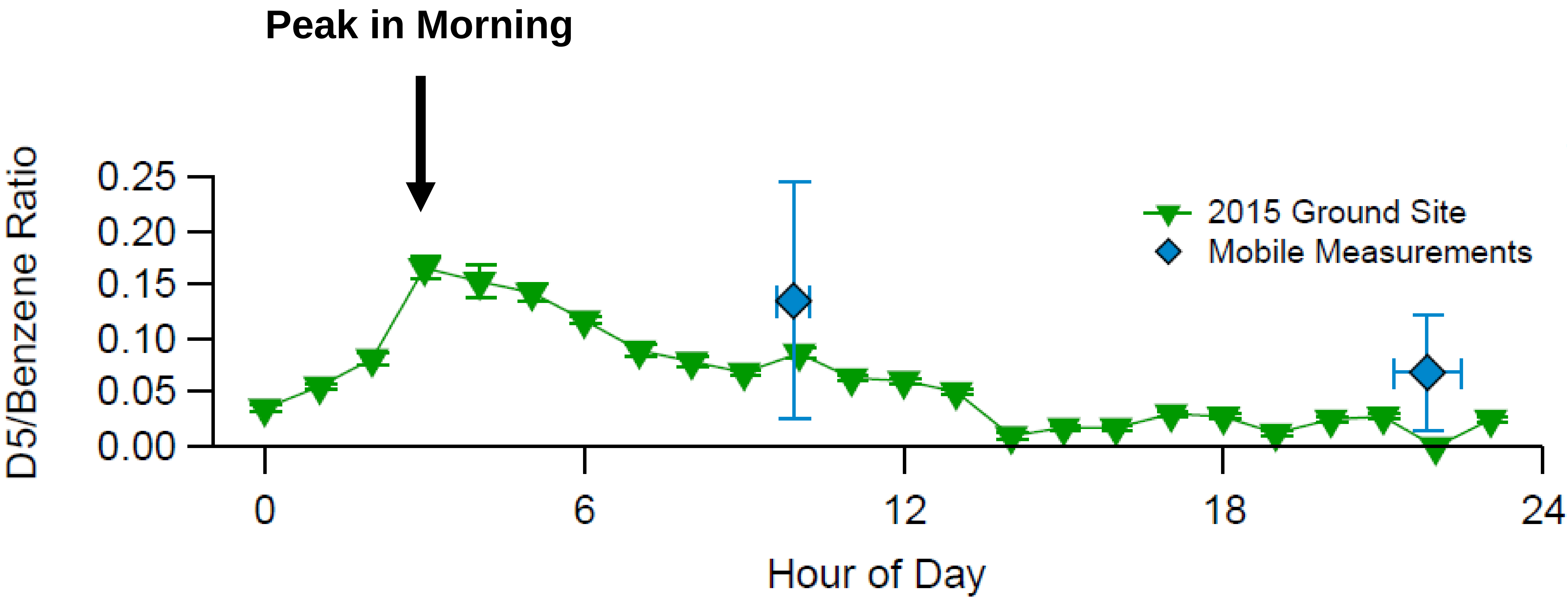
Diurnal Pattern of D5-Siloxane and Benzene



General structure in diurnal pattern similar,
except D5-siloxane peak not as strong as benzene in evening.

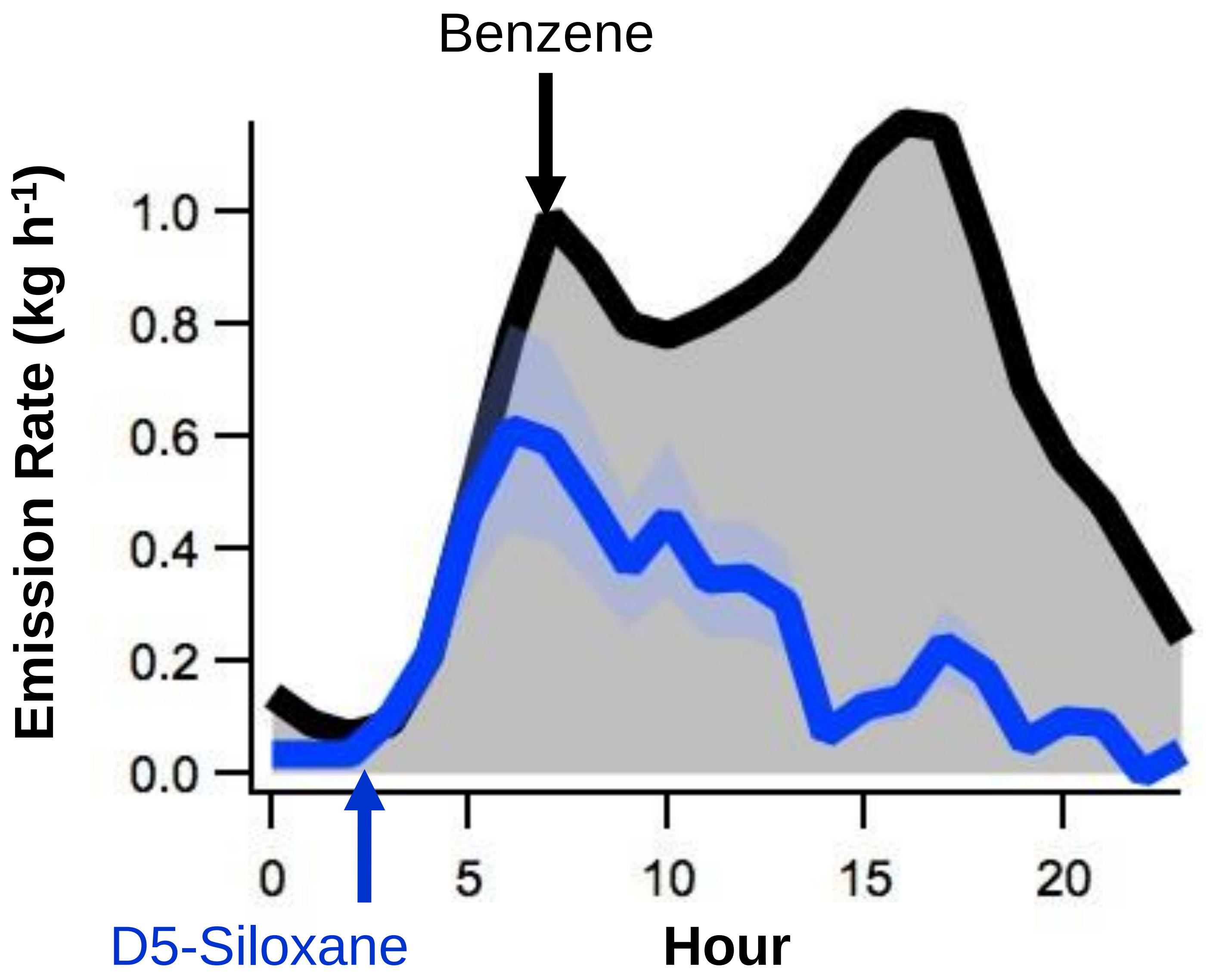
Coggon et al. (*Environ. Sci. & Technol.* 2018)

D5-Siloxane/Benzene Ratio Variable Throughout Day



Coggon et al. (*Environ. Sci. & Technol.* 2018)

Estimated Diurnal Emissions Rate of D5-Siloxane

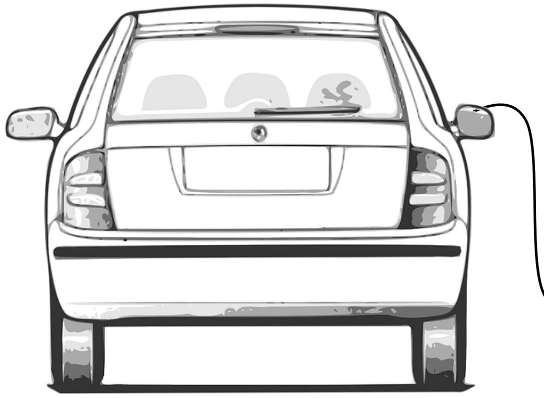


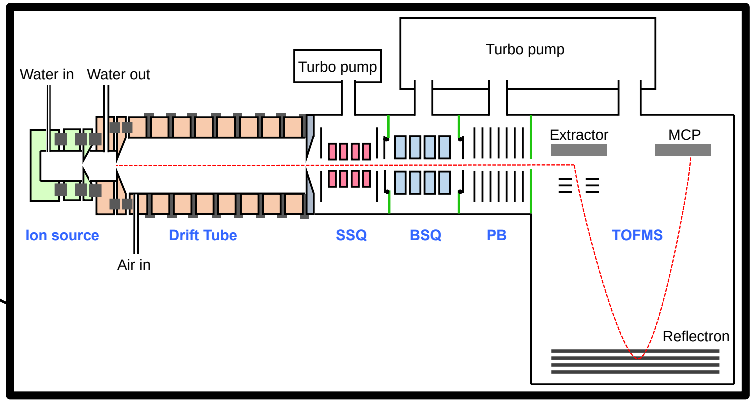
Benzene mostly from gasoline vehicles (morning & evening peaks)

D5-Siloxane from personal care products (morning peak only)

Coggon et al. (*Environ. Sci. & Technol.* 2018)

D5-Siloxane Emitted by People in Cars?





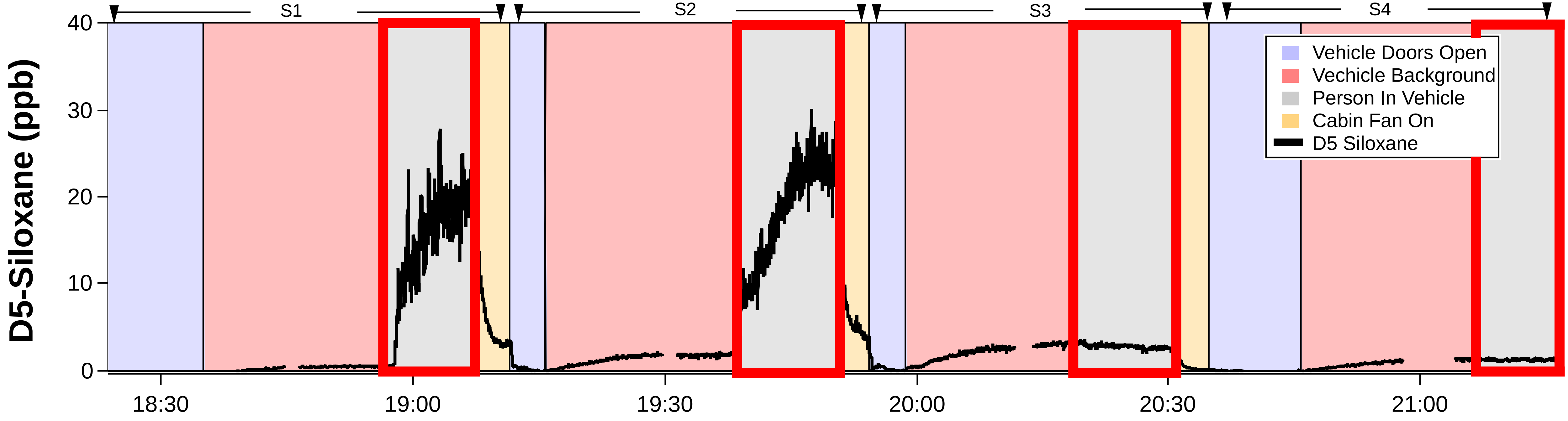
Experiment:

(1) Flush car with ambient air

(2) Measure car background

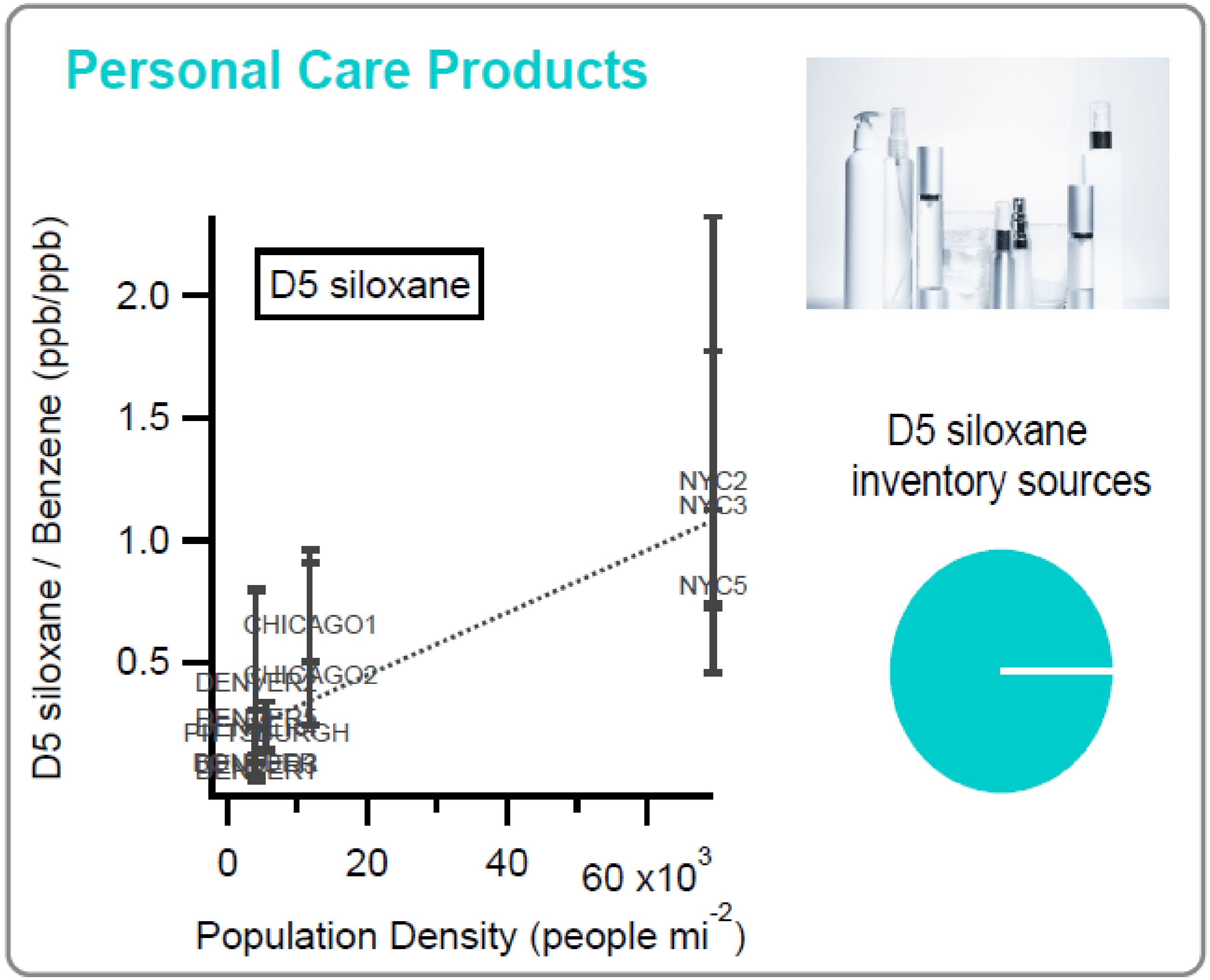
(3) Measure co-worker sitting in car

(4) Turn cabin fan



Coggon et al. (*Environ. Sci. & Technol.* 2018)

Personal Care Emissions Enhanced Relative to Traffic in Denser Cities

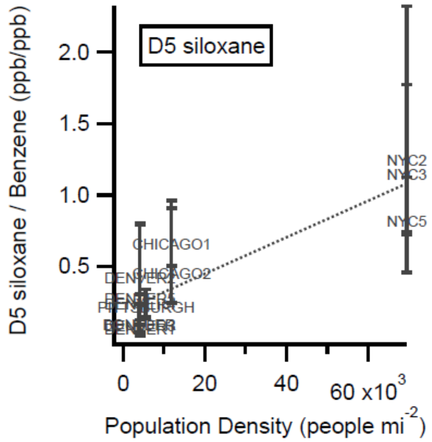


Cites included: NYC, CHI, DEN, PIT

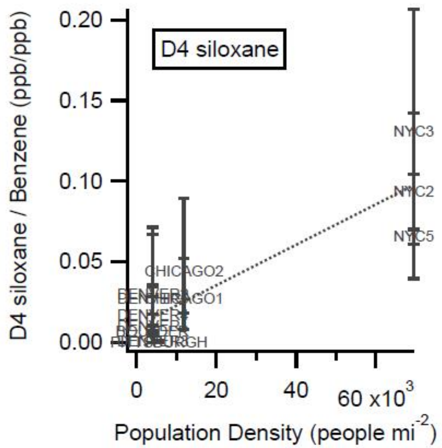
Georgios Gkatzelis
(NOAA)

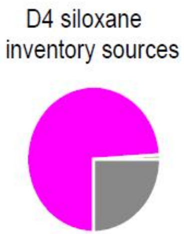
Potential Chemical Markers Identified for Other VCP Source Sectors

Personal Care Products

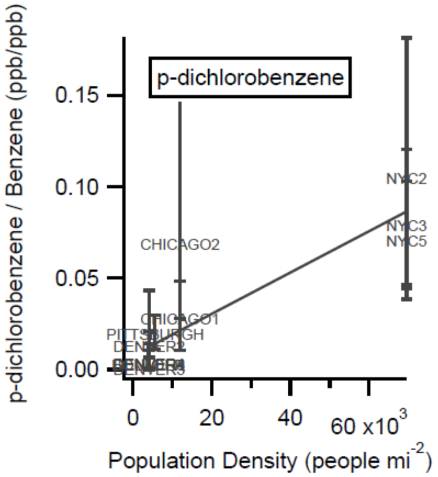


Adhesives

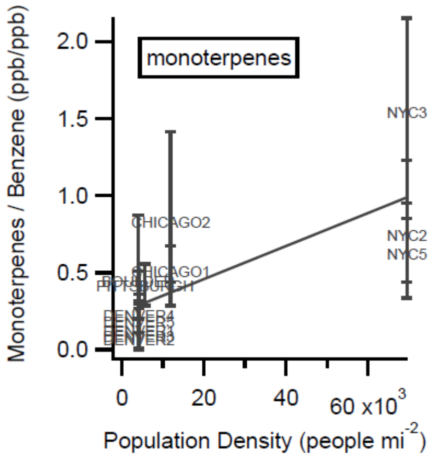




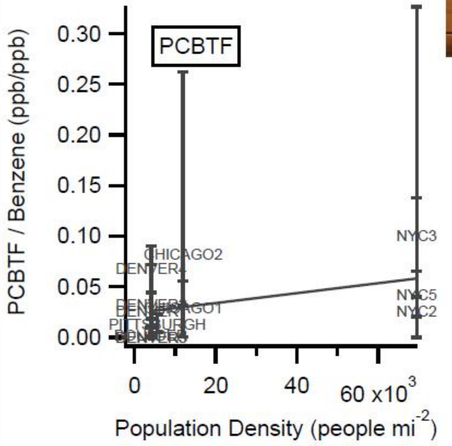
Insecticides

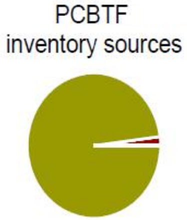


Fragrances

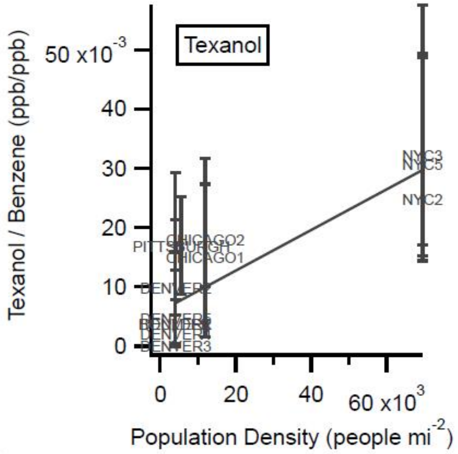


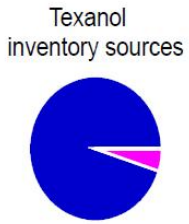
Solvent-Based Coatings





Water-based Coatings





Summary of Chemical Tracers for Detecting VCPs

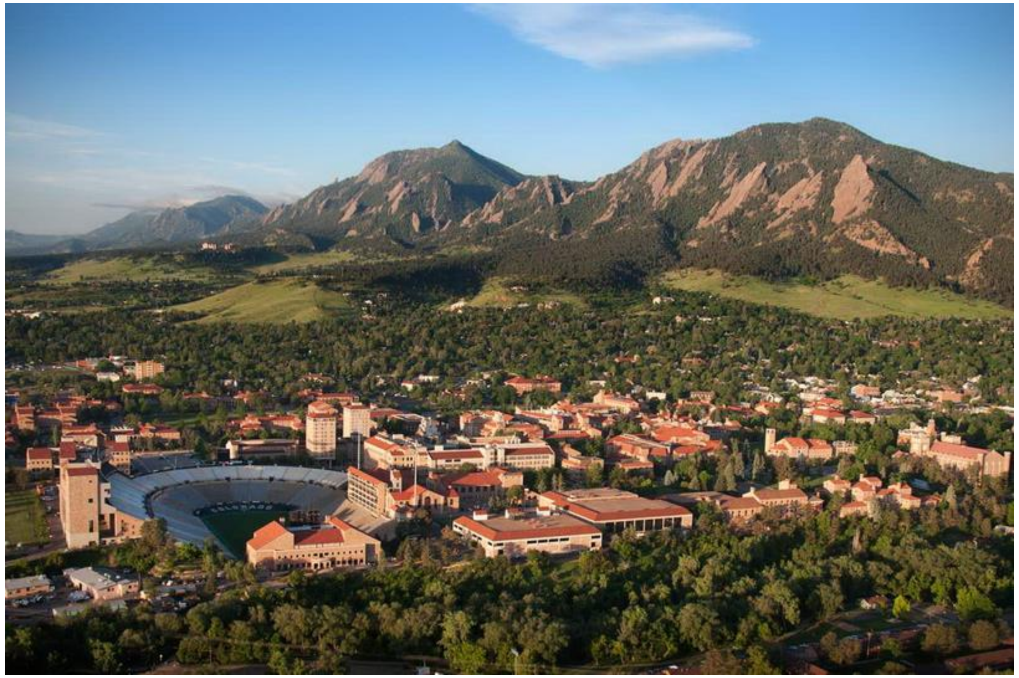
(1) D5-Siloxane useful atmospheric marker of personal care product emissions

- Peak found in morning, then decays exponentially across the day
- D5-Siloxane/benzene ratio enhanced in denser cities

(2) Identifying other potential tracers for VCP sectors

How Important are VCP Emissions in the Biggest US City?

Boulder, CO



Land Area = 64 km^2

Population = 100,000

Commute time ~ 20 min

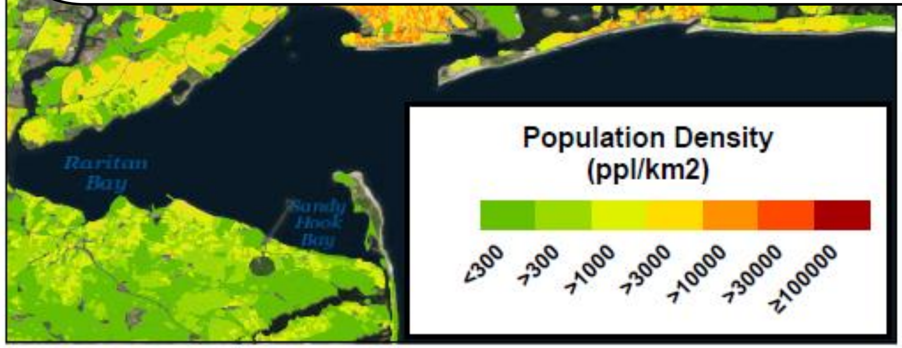
Manhattan, NY

Land Area = 59 km^2

Population = 1,600,000

Commute time ~ 1.5 hr

NOAA Field Measurements in Winter/Summer of 2018



March 5 – 28, 2018

July 6 – 26, 2018

Matthew Coggon

Brian McDonald

Jessica Gilman

Georgios Gkatzelis

Carsten Warneke

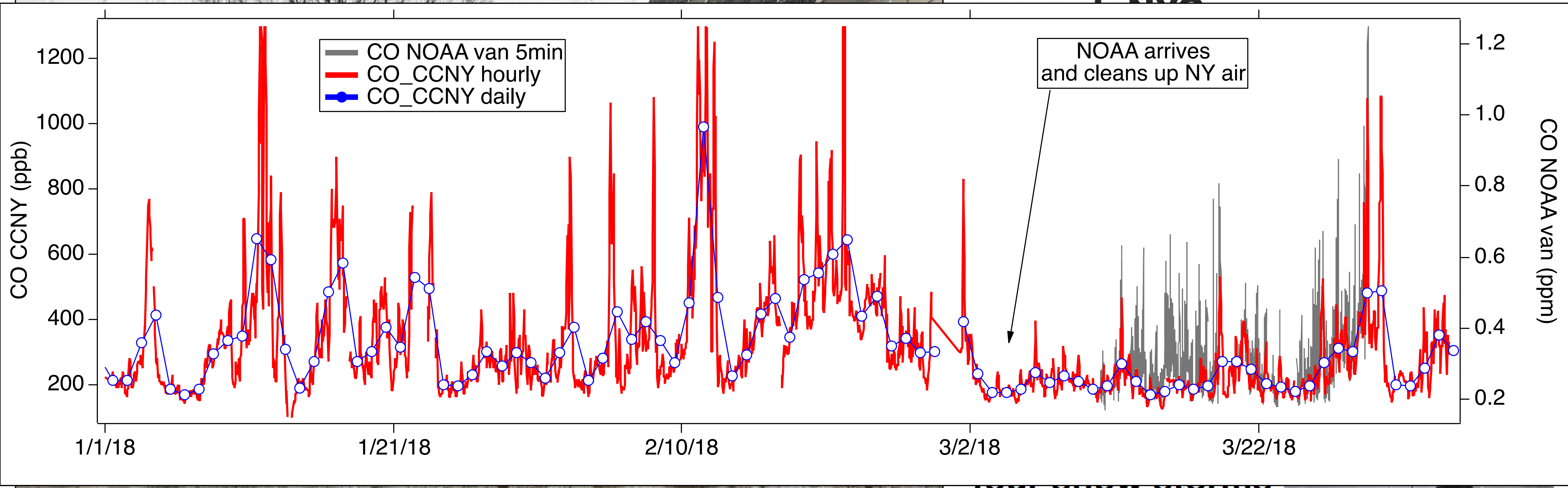
Jeff Peischl

Deployed mobile van with **PTR-ToF-MS, iWAS canisters, CO,** CO_2, CH_4, N_2O

Wintry Conditions = Lack of Biogenic Emissions of VOCs

METRO

Fourth nor'easter in 3 weeks



in four weeks

Yahoo News (3/21/18)

Methods to Quantify New York City VOC Emissions

(1) Quantify “bottom-up” VOC emissions using inventory methods

- Emissions = Activity * Emission Factor

(2) Estimate VOC/CO emission ratios for individual VOC species

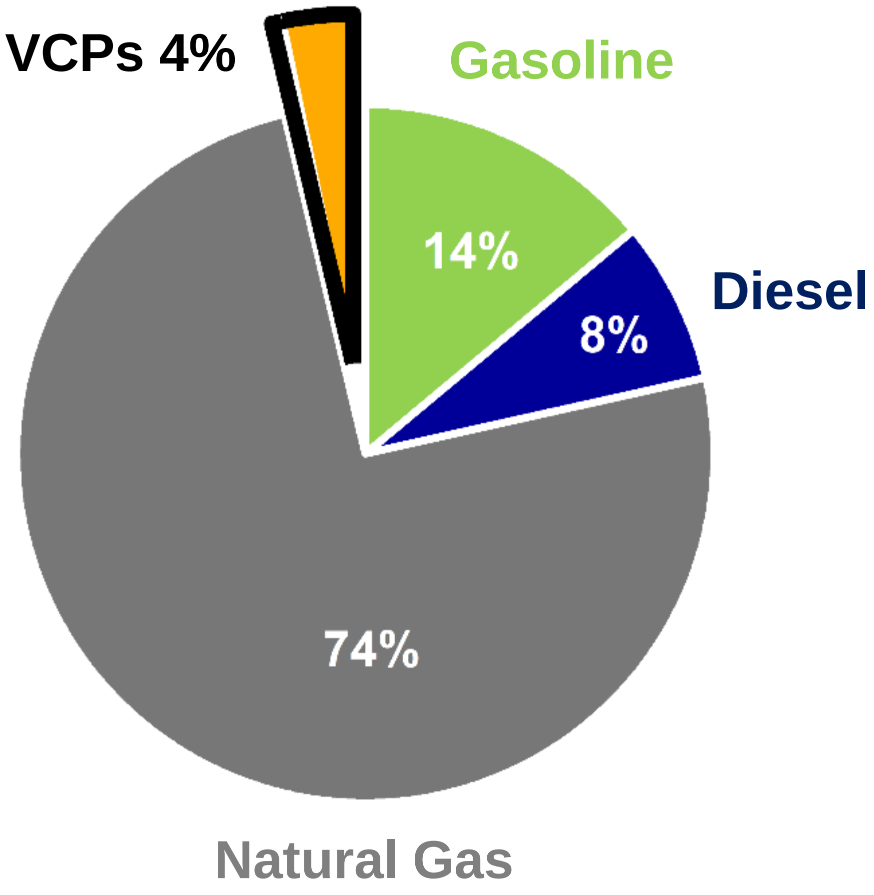
- Controls for effects of atmospheric dilution on ambient concentration data

(3) Compare inventory with ambient VOC/CO field data

- Evaluate with ground site data at City College of New York

Quantifying Fossil Fuel and Chemical Product Use in NYC

Manhattan (Winter 2018)

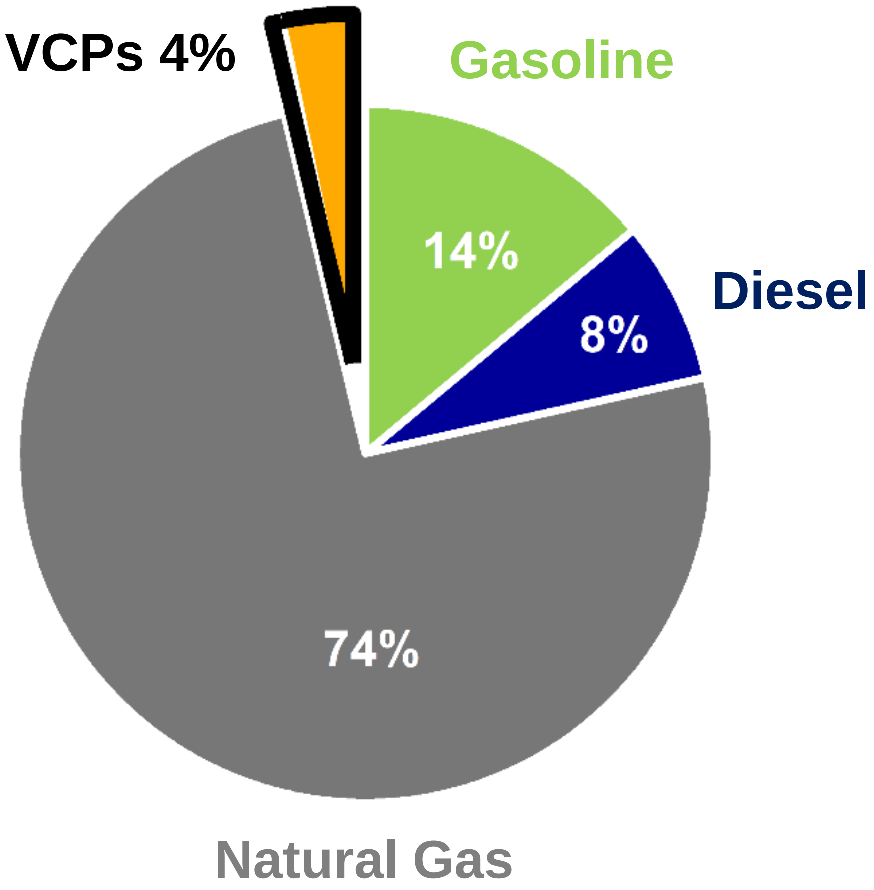


Product Use = 6.6 kg/person/d

- State-level **on-road gasoline** and **diesel** fuel sales allocated to NYC using traffic data [McDonald et al., *ES&T* 2018]
- State-level **off-road gasoline** and **diesel** fuel sales allocated to NYC by population [FHWA, EIA]
- State-level **natural gas** fuel sales by month allocated to NYC by population [EIA]
- Per capita **VCP** use allocated to NYC by population [McDonald et al., *Science* 2018]

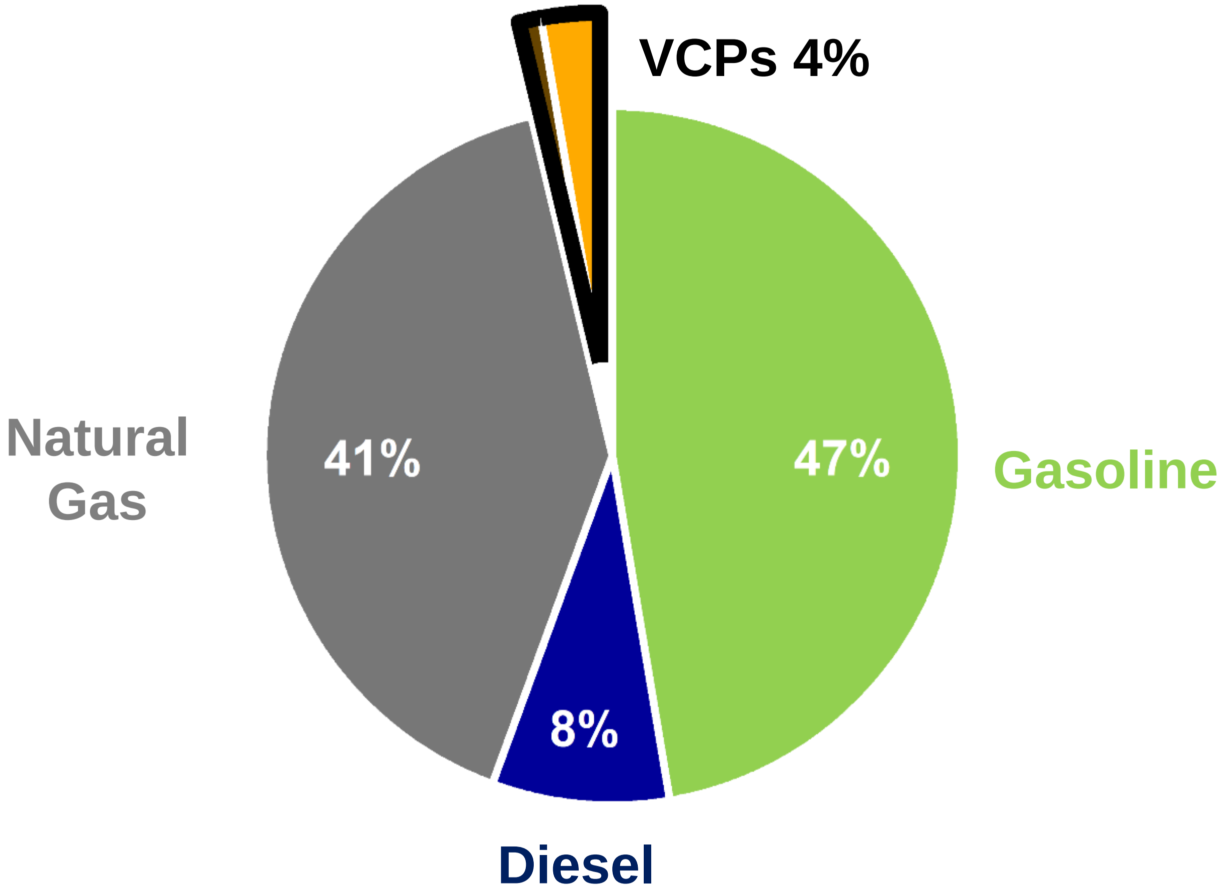
Petrochemical Use Data between NYC and Los Angeles

Manhattan (Winter 2018)



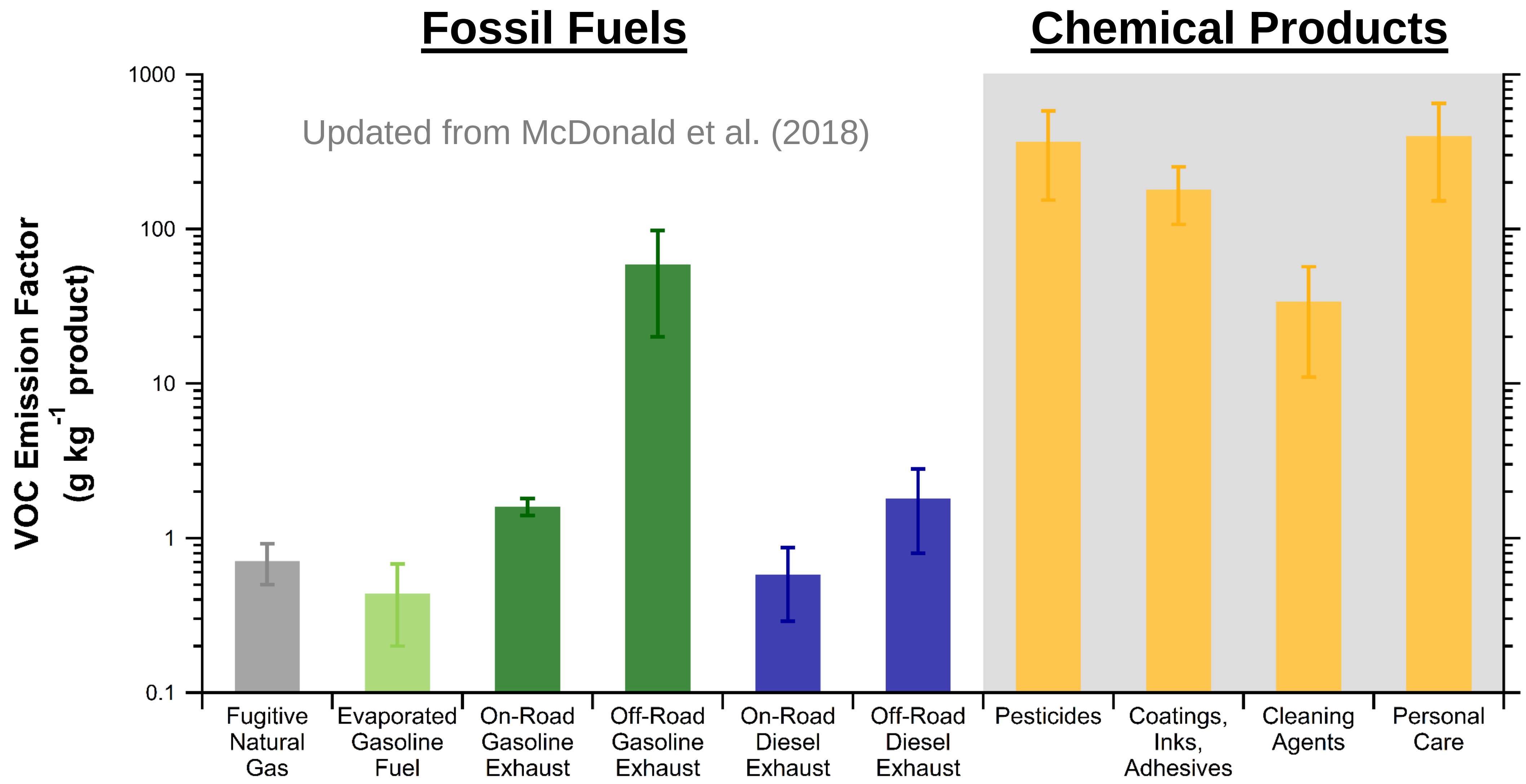
Product Use = 6.6 kg/person/d

Los Angeles (Summer 2010)



Product Use = 6.5 kg/person/d

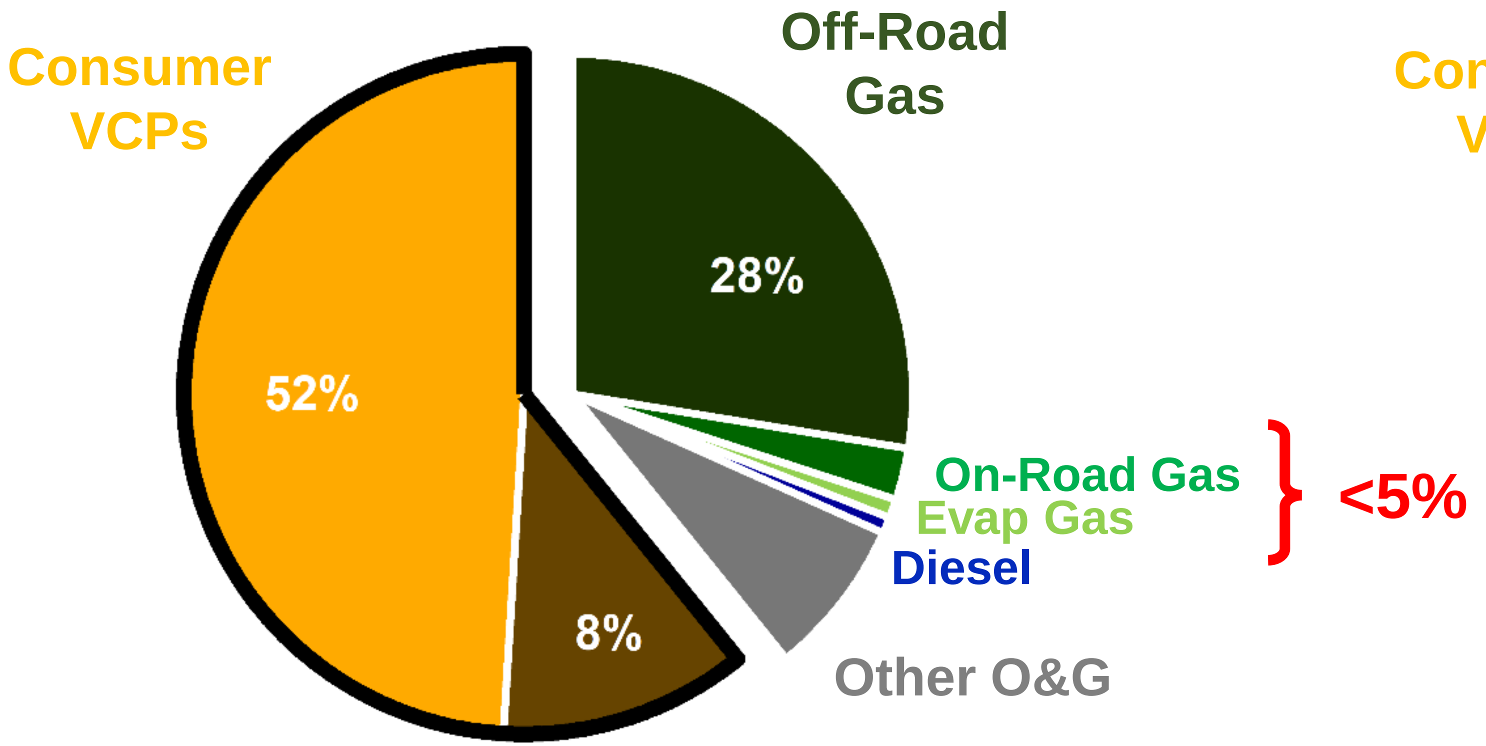
Fossil Fuel vs. VCP VOC Emission Factors (NYC 2018)



Manhattan Sales (g/person/d)	4920 (±250)	920 (±60)	700 (±50)	220 (±110)	430 (±40)	70 (±10)	4.3 (±2.0)	56 (±8)	160 (±40)	28 (±7)

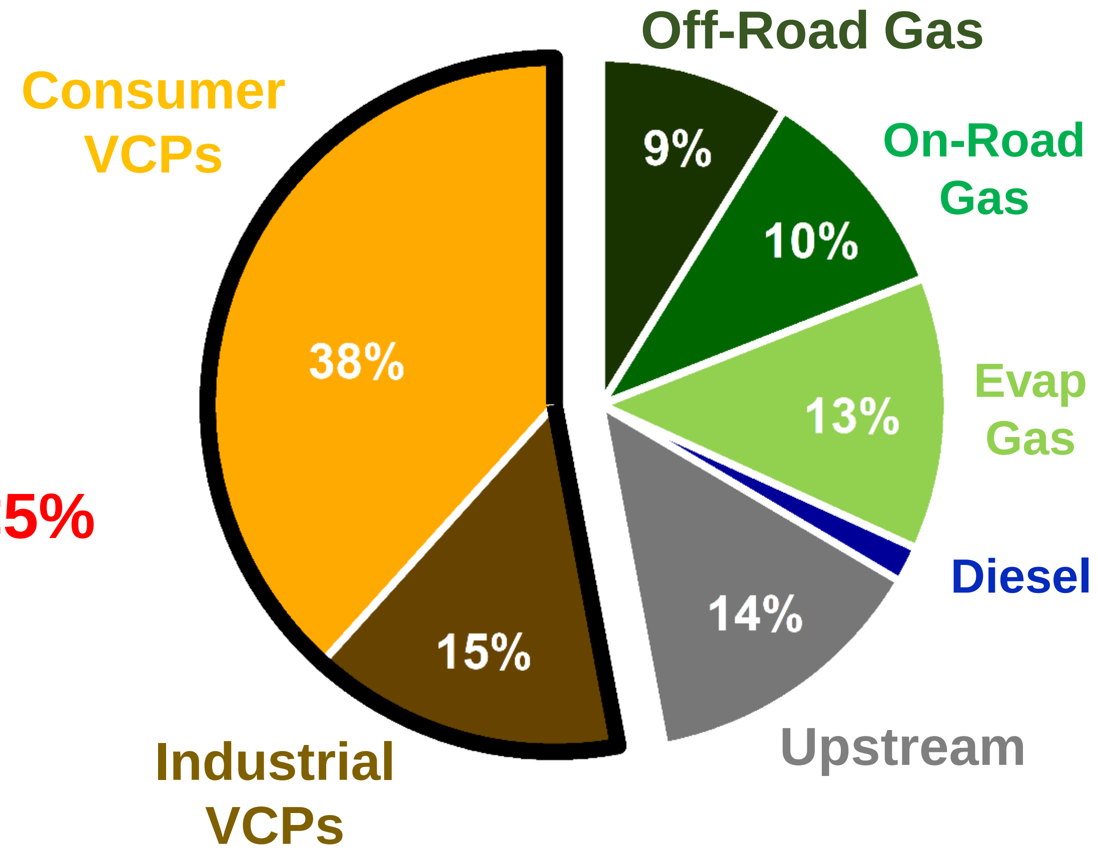
Distribution of Petrochemical VOC Emissions

Manhattan (Winter 2018)



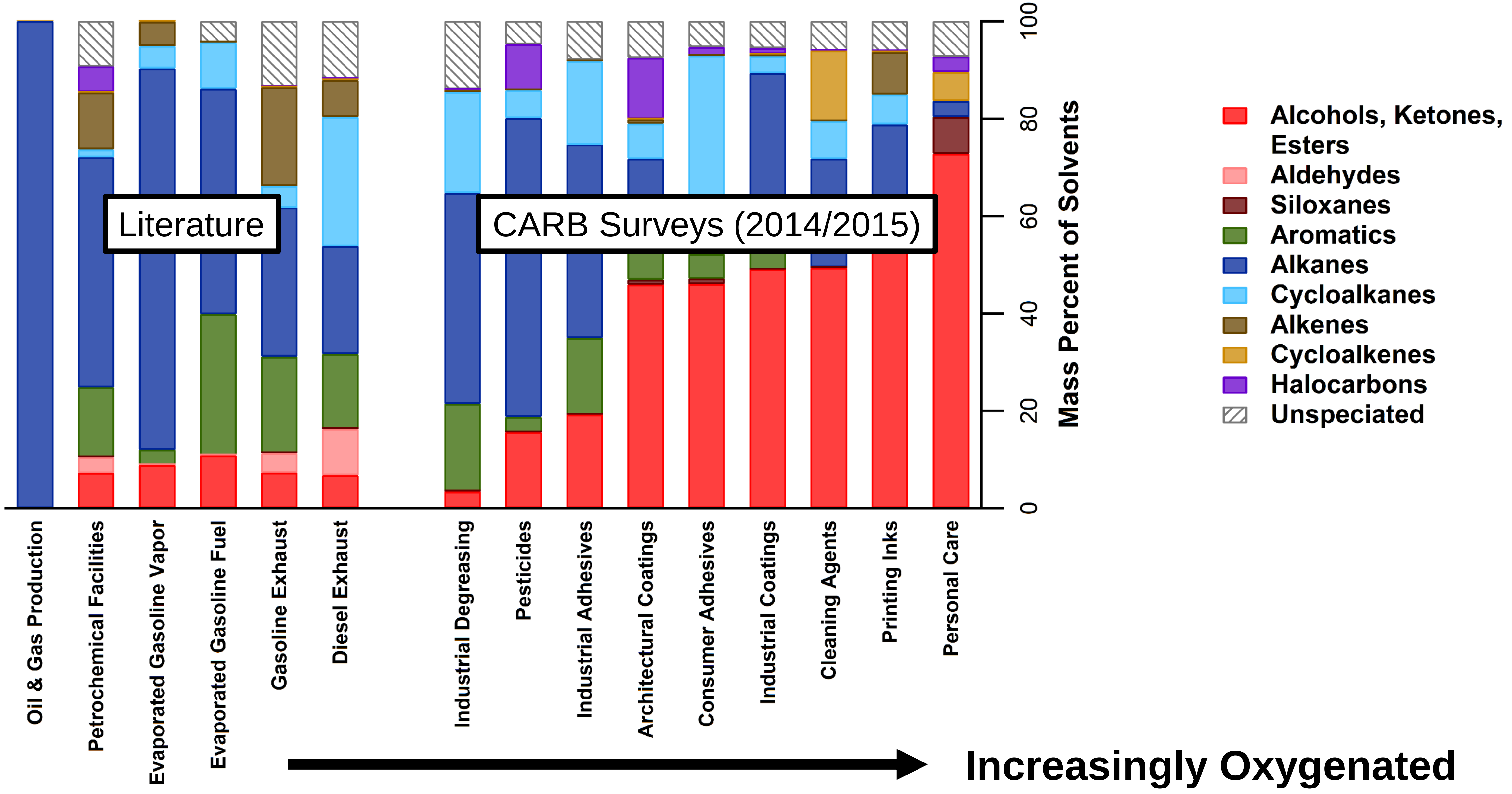
VOC Emissions = 46 ± 12 g/person/d

Los Angeles (Summer 2010)

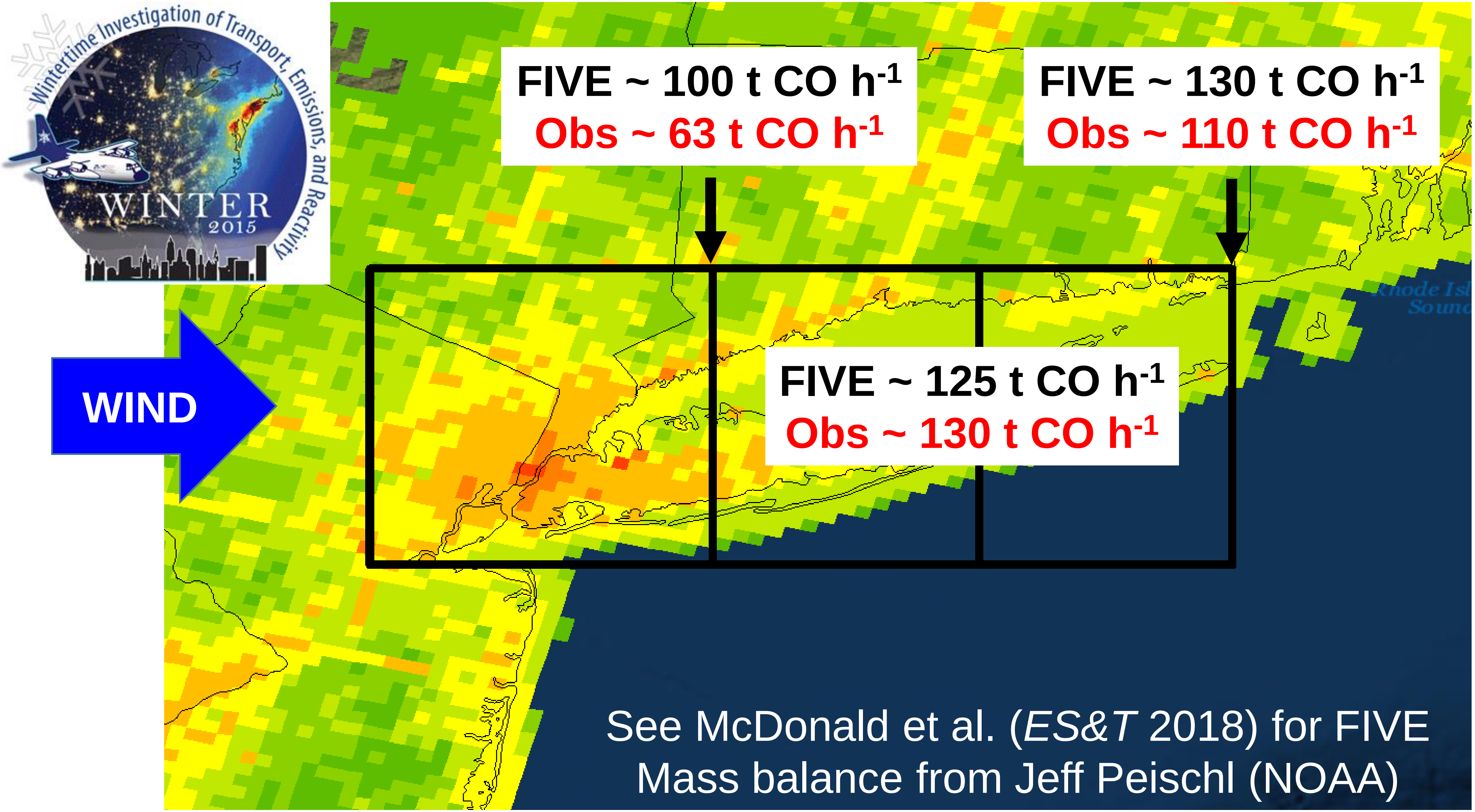


VOC Emissions = 61 ± 9 g/person/d

VOC Speciation Profiles for Fossil Fuels and VCPs

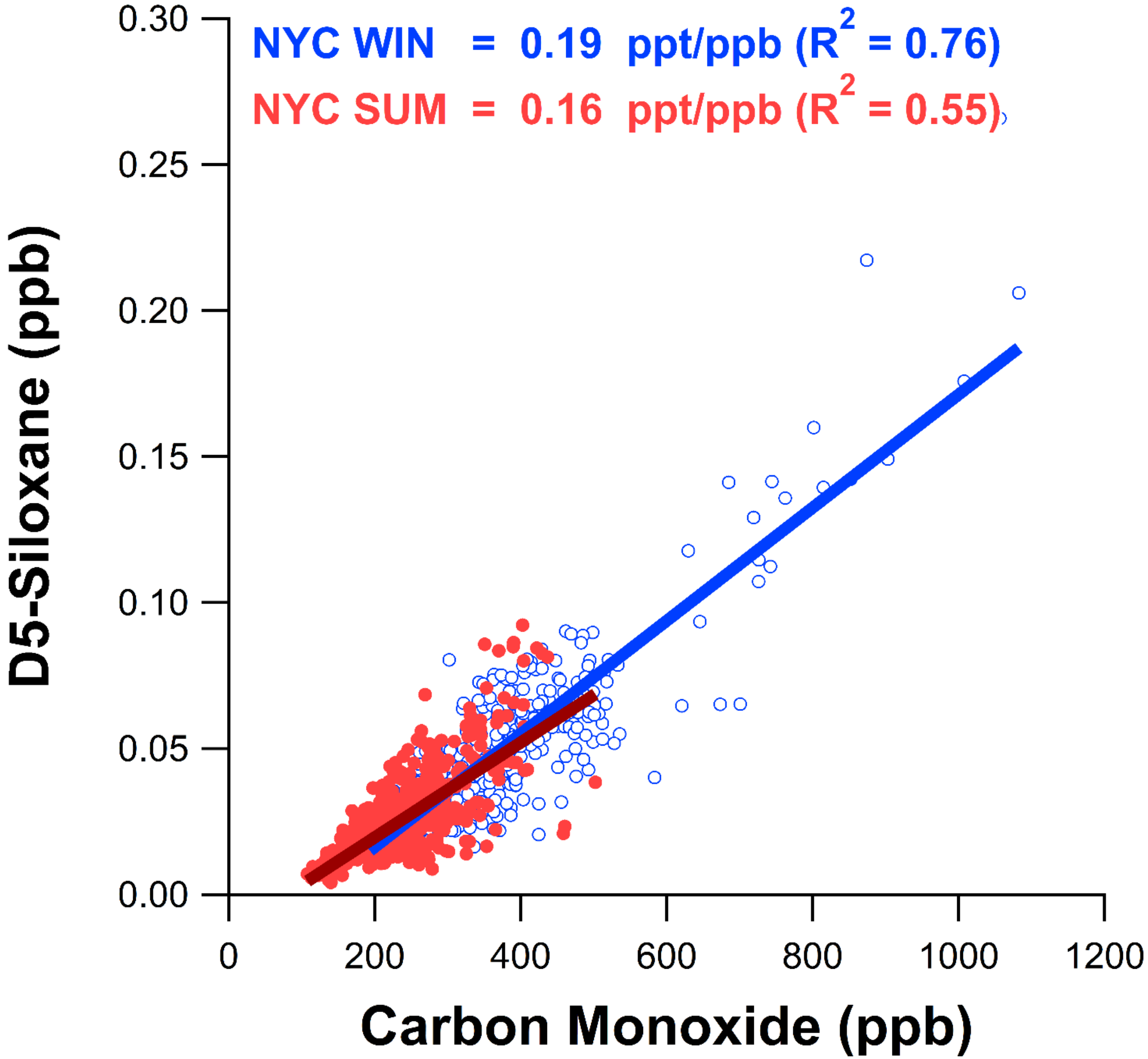


Fuel-Based Inventory of Vehicle Emissions for estimating CO



See McDonald et al. (*ES&T* 2018) for FIVE
Mass balance from Jeff Peischl (NOAA)

Estimating a D5-Siloxane Emission Factor in New York City



New York City (Manhattan only)

CO Emissions = 240 ± 60 t/d

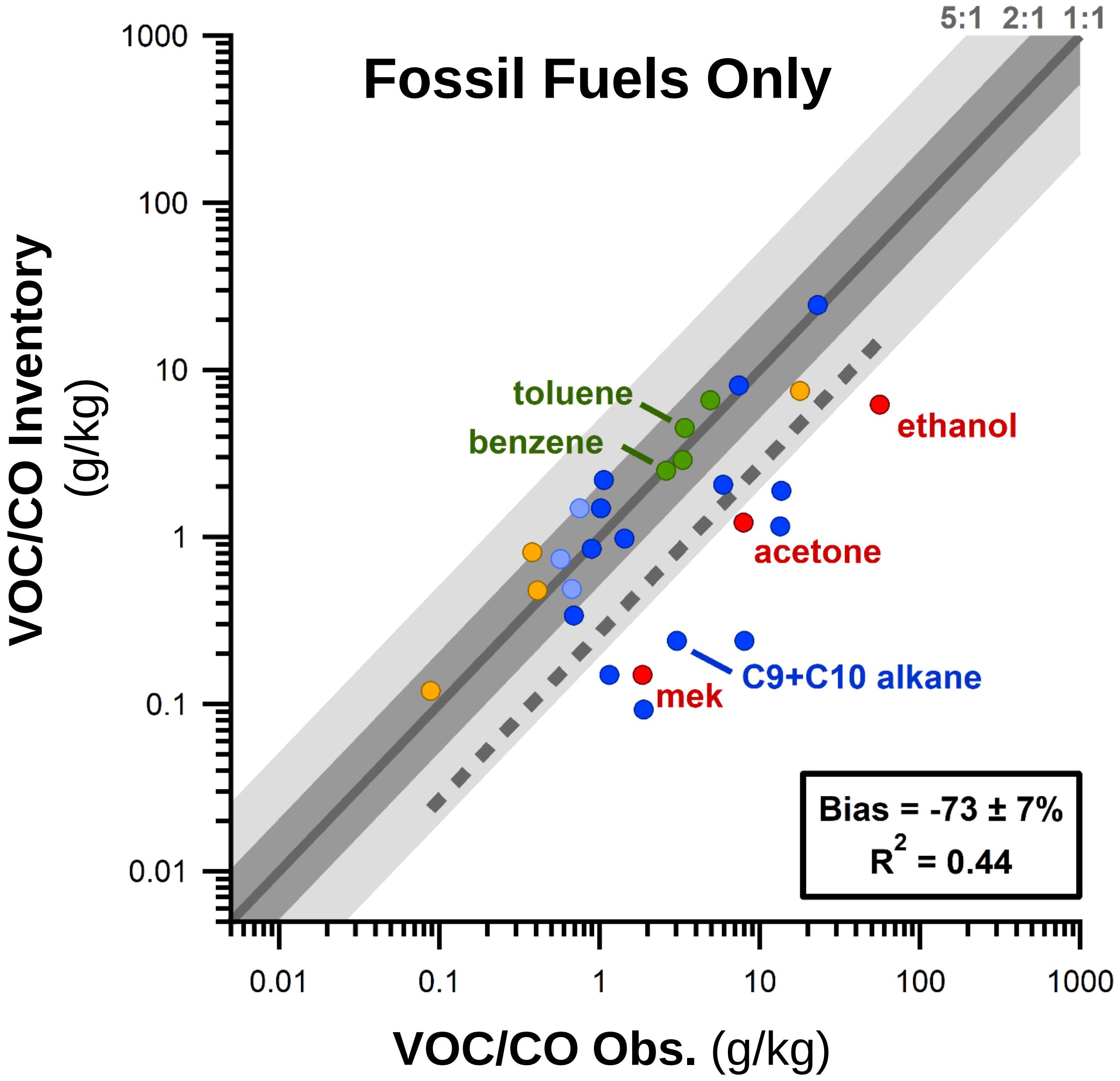
Population = 1.7 million

D5 EF (NYC) = 330 ± 100 mg/person/d

D5 EF (LA) = 390 ± 150 mg/person/d

McDonald et al. (*Science* 2018)

Fossil Fuels Alone Cannot Explain Ambient VOC Levels in Manhattan

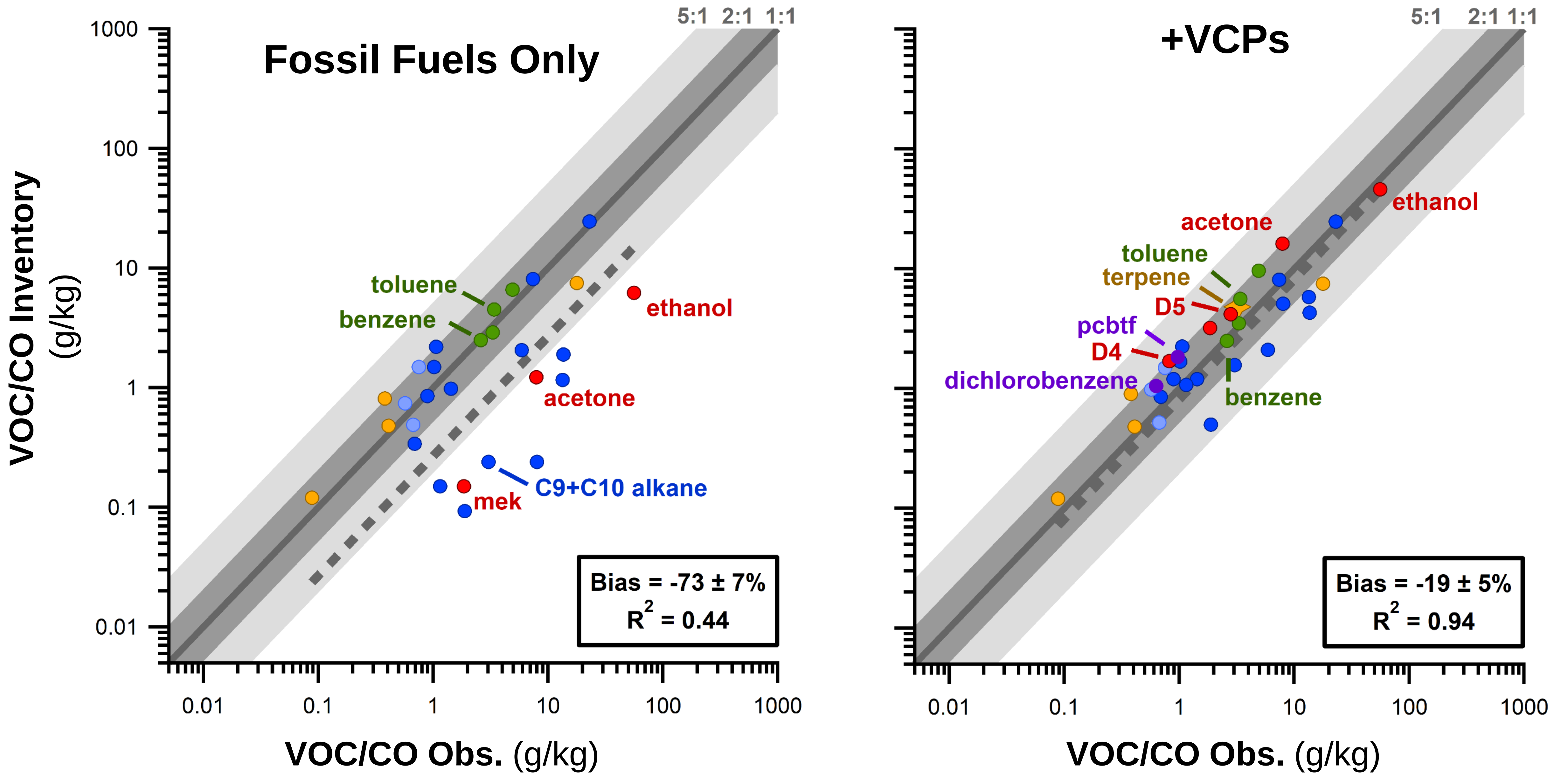


30+ VOCs measured by…

GC-MS analysis of iWAS canisters
(alkanes, cycloalkanes, alkenes, aromatics)

In-situ PTR-ToF-MS
(oxygenates, terpenes, select halocarbons)

Need VCP Emissions to Explain Ambient VOC Levels in Manhattan



Summary of NYC VOC Field Measurements

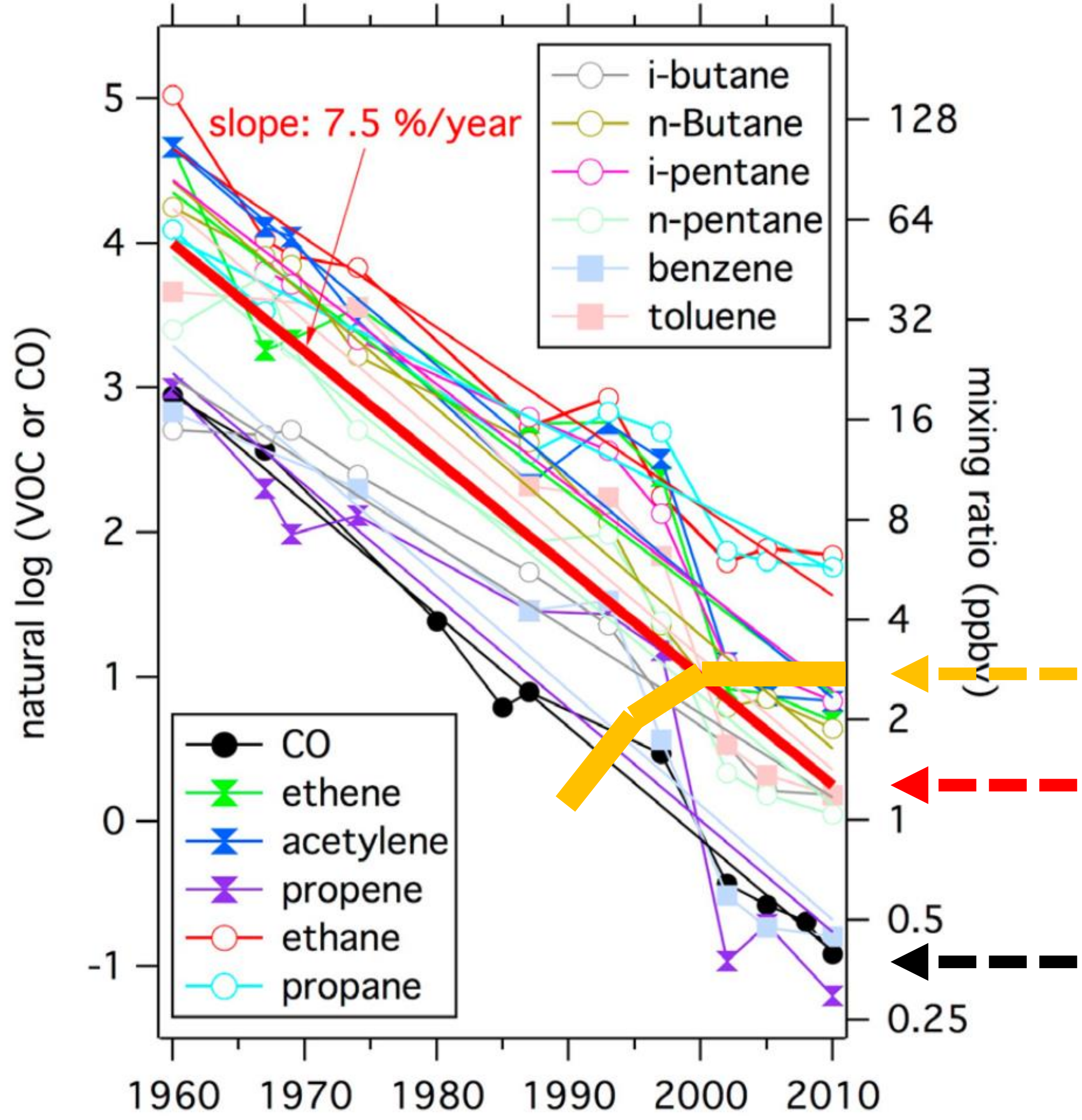
(1) Quantified petrochemical VOC emissions for NYC using same methodology as Los Angeles

- VCPs account for **over half** of the petrochemical VOC emissions in NYC

(2) Evaluated VOC inventory with ambient field measurements

- VCP emissions needed to explain ambient levels of VOCs (**R^2 ~ 0.94**)
- Can explain ambient levels of chemical tracers for VCPs

Identifying Atmospheric Constraints on Trends in VCP Emissions



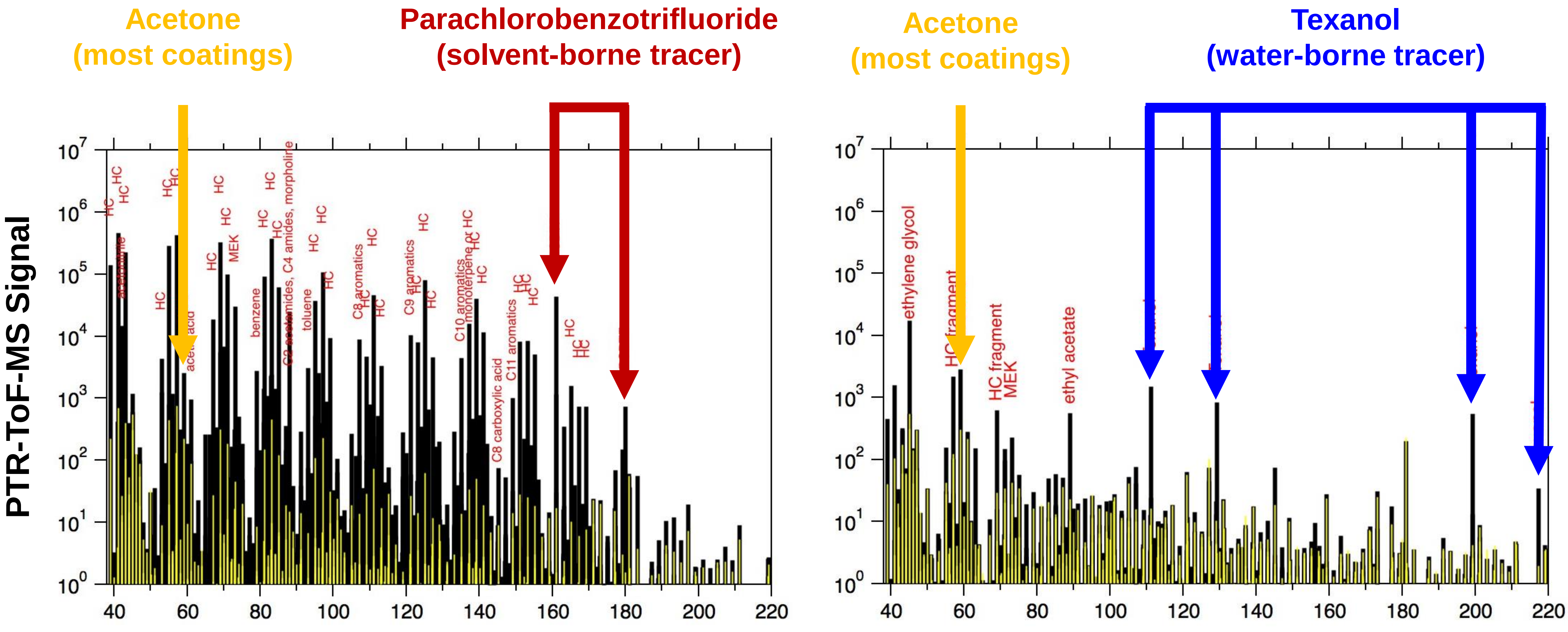
Acetone Increasing → Flat Trend

Gasoline VOCs Decreasing Rapidly

CO Decreasing Rapidly

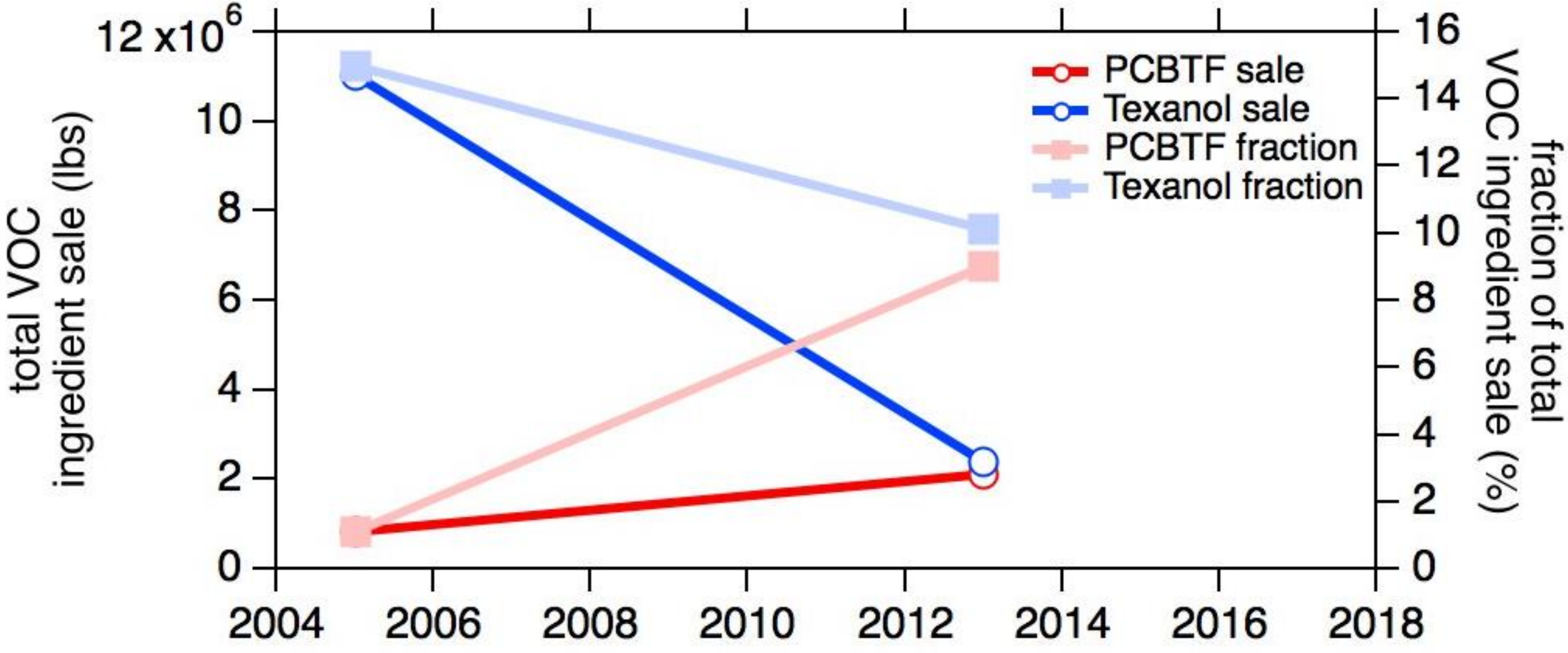
Warneke et al. (*J. Geophys. Res.* 2012)

PTR-ToF-MS Mass Spectra of Various Coatings



Solvent-borne Water Stain >> Low VOC Paint

Trends in Two Tracers for Coating-Related Products



https://www.arb.ca.gov/coatings/arch/survey/2005/survey.htm

Concluding Remarks

(1) Ambient measurements in New York City and Los Angeles indicate that VCPs are ubiquitous and significant source of urban VOCs.

(2) Measurements of VCP markers now possible with advancements in VOC instrumentation → improve confidence in emission inventories